QUEEN'S UNIVERSITY BELFAST

PREPARATION OF GREEN NON-IONIC SURFACTANTS FROM 2,3-EPOXY-1-PROPANOL

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Abstract

Non-ionic surfactants are important materials for use in textile, cosmetic and agricultural fields and have a large share of the overall surfactant global market. In addition, the use of bio raw materials in their production is important for sustainability aspects and can lead to “green” and differentiated products in the market. In this work, glycidol has been used as a starting material to produce non-ionic surfactants. Glycidol can be produced from glycerol carbonate, an important chemical intermediate which is synthesised via transesterification from glycerol, a by-product of biodiesel manufacture, and dimethyl carbonate.

All of the products presented in this work were prepared by reacting glycidol with a range of fatty alcohols. High yields were achieved after optimising different experimental conditions e.g. addition rate, reaction time, temperature and catalyst. Highly hydrophilic polyglyceryl ether-based non-ionic surfactants were obtained by increasing the ratio of glycidol to alcohol. Most of these materials showed high solubility in water and good surfactant properties including low critical micelle concentrations (CMC), low surface tension at the CMC point and good foaming characteristics which make their market prospects very favourable.

Key words: non-ionic surfactants (NIS), Glycidol (EP), poly(glyceryl) ethers, critical micelle concentration (CMC), foaming ability.

Symbols and abbreviations

AEO	Fatty alcohol ethoxylate
APEO	Alkylphenol ethoxylates
CMC	Critical micelle concentration
CP	Cloud point
C_6	1-Hexanol
C_8	1-Octanol
C_{10}	1-Decanol
C_{12}	1-Dodecanol
C_{14}	1-Tetradecanol
C_{16}	1-Hexadecanol
C_{18}	1-Octadecanol
DMC	Dimethyl carbonate
DMF	Dimethylformamide
EP	Glycidol, 2,3-Epoxy-1-propanol
GLC	Glycerol carbonate
GLT	Green Lizard Technologies
$La(OTf)_3$	Lanthanum(III) trifluoromethanesulfonate
NIS	Non-ionic surfactant
QUILL	Queen's University Ionic Liquid Laboratories
^1H NMR	Hydrogen/proton nuclear magnetic resonance spectroscopy

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1 Context and project aims

1.1 Context

There is much focus on the use of renewable resources instead of petrochemical raw materials for producing various types of chemical products as part of the sustainable development goals in the chemical industry. In addition, the use of biofuels continues to increase, that renewable power (excluding hydro) grew by 14.1% in 2016, below the 10-year average, but the largest increment on record (53 million tonnes of oil equivalent or Mtoe),[1] helping to reduce greenhouse gas (GHG) emissions and the reliance on petroleum products derived from fossil fuels. Biodiesel will play an important role in the future due to government mandates and initiatives on renewable fuel policies.[2] Biodiesel (fatty acid methyl ester) produced from oils is an example of renewable fuel,[3] and production has been increasing in recent last years (Figure 1). Biodiesel is produced by the transesterification process of vegetable oils with methanol, producing approximately 10 wt% of glycerol as by-product, with a purity of around 50%–55%.[4]

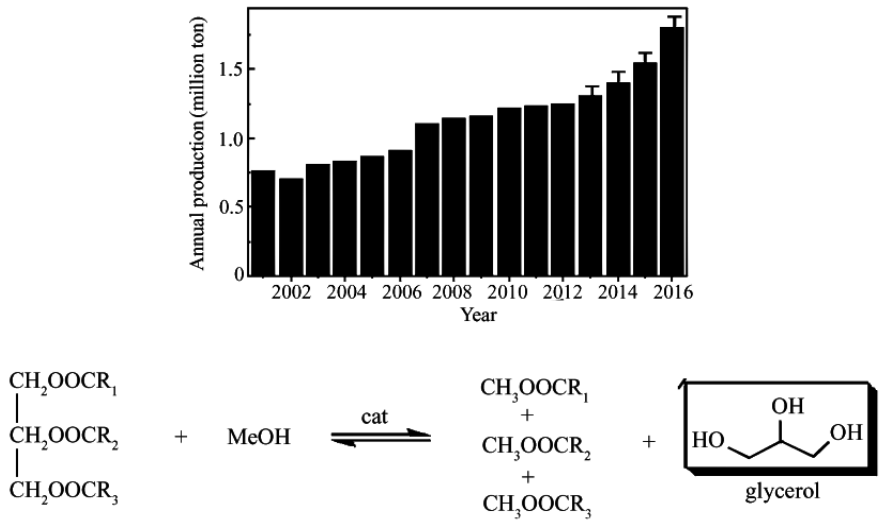


Figure 1 Growth trend of glycerol as a by-product from bio-oils[5]

As biodiesel production increases there will be a glut in crude glycerol produced as a waste by-product. According to a market report published by Transparency Market Research,[6] the global demand for glycerol is expected to reach 3,060.4 kilo tons by 2018, growing at a CAGR (Compound Annual Growth Rate) of 6.3% from 2012 to 2018. In terms of revenues, glycerol demand is expected to reach $2.1 billion in 2018, growing at a CAGR of 7.7% from 2012 to 2018.[7] Therefore, great efforts have been focussed in the valorisation of glycerol by its conversion into value-added chemicals.

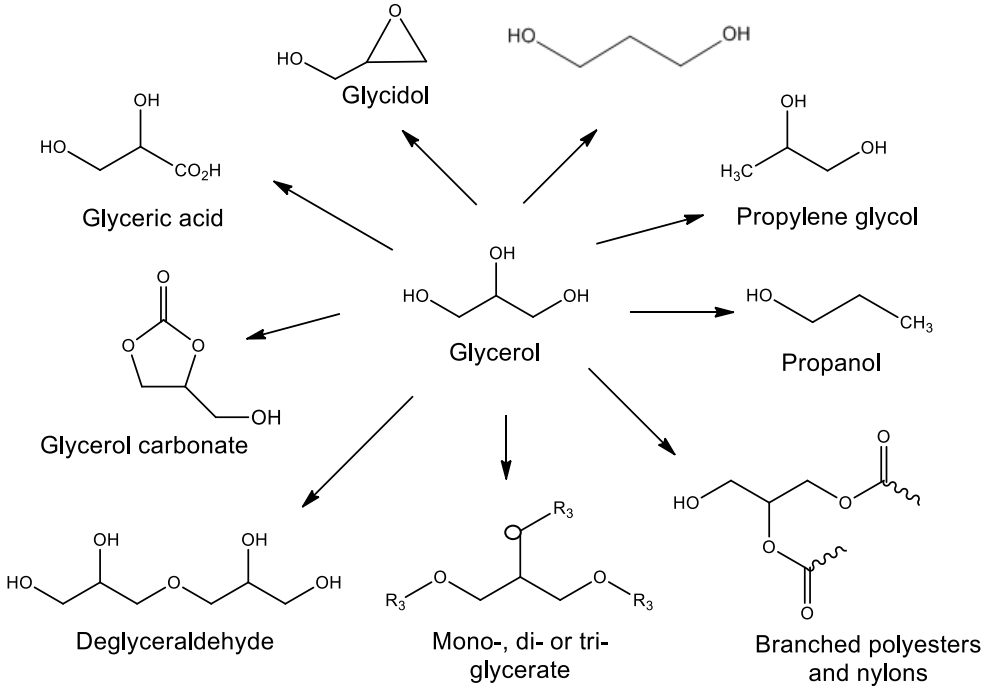


Figure 2 A scheme of some possible applications about glycerol[8]

Glycerol is used to produce glycerol carbonate (GLC), an important chemical intermediate of industrial interest (Figure 2). For example, thermal and catalytic decarboxylation of GLC results in formation of 2,3-epoxy-1-propanol (glycidol/EP) and CO_2 (Figure 3). During my research, GLC and EP were used as starting materials to produce non-ionic surfactants.

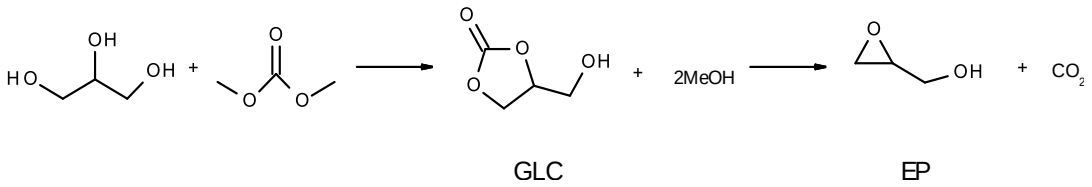


Figure 3 Production of glycerol carbonate(GLC) and glycidol(EP) from glycerol and DMC

In 2014, the world market for surfactants reached a value of more than 33 billion US-dollars.[9] During the last 35 years, non-ionic surfactants have increased their market share reaching almost 40% of the total surfactant manufacture in the world.[10] The production of non-ionic surfactants from fatty alcohols is particularly important due to their outstanding performance when compared to other types of surfactants, including lower sensitivity to electrolytes which enables them to be used in hard water conditions. In addition, they show low toxicity together with ease of manufacture.[11]

1.2 Project aims

In my research, the synthesis of non-ionic surfactants from glycidol and glycerol carbonate has been undertaken. Glycerol carbonate and glycidol can both react with primary alcohols to give alkyl glyceryl ethers which find applications as non-ionic surfactants (Figure 4).

The proposed non-ionic surfactants synthesis routes include the etherification of alcohol and phenol with different ratios of glycidol or glycerol carbonate with different types of catalysts. However, selective and efficient catalysts are needed in order to optimise both routes.

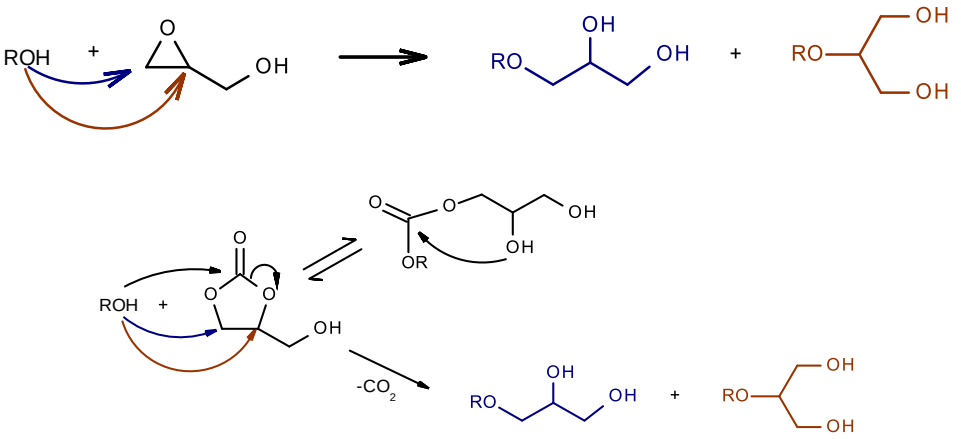


Figure 4 Reaction of alcohols with glycidol and glycerol carbonate to give alkyl glyceryl ethers

There is scant information in the literature about my approach from glycidol and only few researches in the world have been published on this topic, most papers focus on alkyl glyceryl ethers as non-ionic surfactants synthesis from glycerol (Figure 5) because of its cost is lower compared to GLC and EP.[1213] Generally, the conversions are poor. Thus, a greener process which ensures high GLC/EP conversions to produce NIS derivatives from fatty alcohols while keeping the cost low is highly desirable.

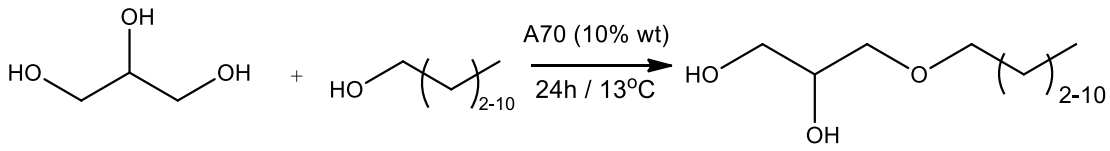


Figure 5 Catalytic etherification of glycerol with fatty alcohols over A70 (A70,10 wt% Amberlyst 70 corresponding to 1.1 mol% H^+) [12]

The products presented in my research are new and have not been widely produced in the market so it was necessary to measure their main properties as surfactants, including critical micelle concentration (CMC), foaming abilities etc.

2 Introduction

2.1 Glycerol Carbonate

At present, the chemical conversion of bio-glycerol has become an important topic, especially the catalytic chemical conversion of glycerol due to its ready availability. Glycerol carbonate (GLC) as one example of glycerol conversion, has dual functionality in the molecule, with both reactive alcohol and carbonate groups. GLC is usually produced by the transesterification of glycerol with linear carbonic esters alongside the corresponding alcohols in the presence of a basic catalyst (Figure 6). For my work, all the GLC was synthesised using dimethyl carbonate (DMC) as the carbonylation agent in the transesterification reaction with glycerol under a furnace temperature of 250 °C. The main advantage of this methodology is the use of a green reagent such as DMC, which also has exceptional properties as the reduction of total emissions of hydrocarbons, carbon monoxide and formaldehyde in automobile exhaust gas e.g. in US DMC can replace methyl tert-butyl ether as a gasoline additive.[14] It is also a multi-functional building block in organic synthesis.

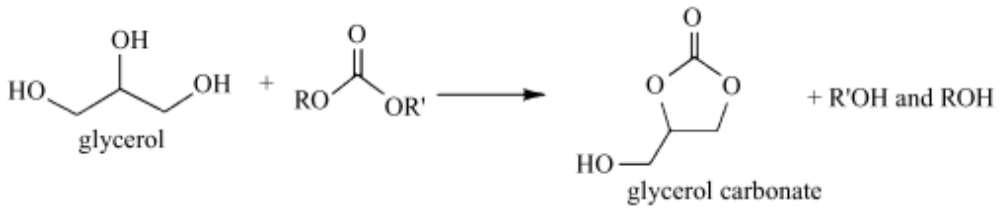


Figure 6 GLC by glycerol transesterification

GLC (molecular formula: $C_4H_6O_4$) is a stable, colourless liquid (at room temperature). GLC is an uninflammable, water-soluble, readily biodegradable, nontoxic, and viscous (85.4 mPa·s at 25 °C) liquid with a very low evaporation rate (boiling point 110−115 °C at 0.1 mmHg). It is noteworthy that GLC is a multifunctional synthetic molecule and as noted above can undergo several types of reactions due to the presence of both hydroxyl and carbonyl functional groups in the molecule, such as nucleophilic

substitution reaction.[15] GLC can be used in medicine, cosmetics, bio-lubricants, solvents.

2.2 Glycidol

Glycidol (chemical formula:$C_3H_6O_2$) is colorless, slightly viscous liquid and an organic compound that contains both epoxide and alcohol functional groups, whose melting point is -54°C.[16] It is soluble in water, alcohol, ether, ketone, chloroform, benzene, dimethyl formamide, and almost insoluble in aliphatic and alicyclic hydrocarbons.

Glycidol is typically synthesized by epoxidation of allyl alcohol using hydrogen peroxide in the presence of a lithium, tungsten or vanadium catalyst (Figure 7) or by the reaction of epichlorohydrin with a strong base which is the most common industrial process.[17]

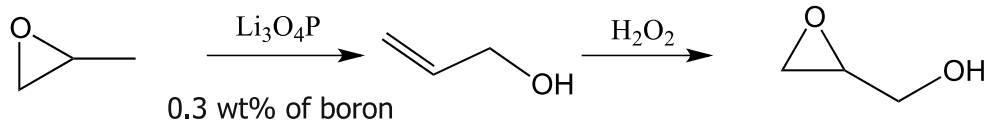


Figure 7 Traditional EP synthesis routes from allyl alcohol[18]

In the first method (Figure 7), Glycidol can be obtained by epoxidation of allyl alcohol with hydrogen peroxide or peracetic acid. When using peracetic acid as epoxidizing agent, the reaction is fast and exothermic producing many by-products e.g. glycidyl acetate which make distillation separation difficult. These are the main reasons this particular route is not favoured by industry.[19]

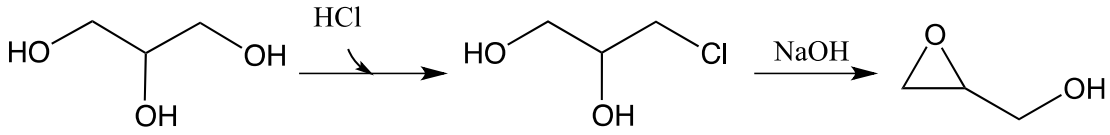


Figure 8 Traditional EP synthesis routes from 3-Chloro-1,2-propanediol

In the second method (Figure 8), glycidol can be produced from 3-chloro-1,2,propandiol reacted in the presence of base at about 0 °C. Pure glycidol can be obtained from the reaction product after removing the salt followed by distillation under reduced pressure.[20]

However, waste streams are expensive to treat therefore, my green synthesis method (Figure 8) targets glycidol from glycerol and DMC. Essentially glycerol carbonate can be converted to (EP) with modest temperatures and low pressures (Figure 9).[21,22]

In comparison to other methods of synthesis, this route is relatively cost effective and uses less hazardous chemicals.

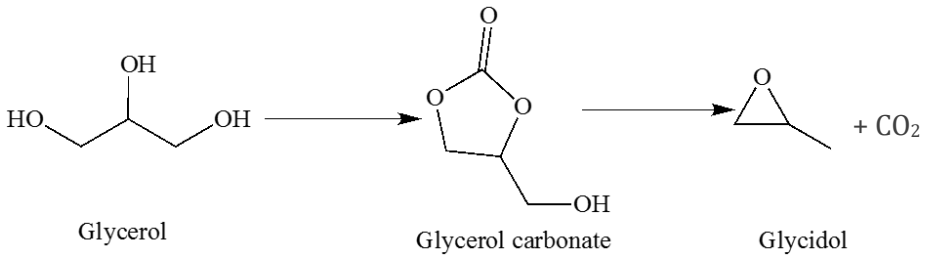


Figure 9 Simple reaction scheme for transesterification of glycerol followed by decarboxylation to CO_2

In 1956, glycidol was only used for research purposes,[23] but in 1978 it started to be used in the preparation of glycidyl and glyceryl ethers and esters in the pharmaceutical industry[24] and as a disinfectant in pharmaceuticals.[25]

Nowadays, glycidol is mainly used as epoxy resin diluent, resin and fiber modifier, protein-containing food preservatives, drugs and beer fungicides, refrigeration system desiccant and aromatic extraction agent and as raw materials for speciality

intermediates.[26,27]

Glycidol has become an important intermediate in the production of functional epoxides. For example, glycidol reacted with phosgene provides 2,3-epoxypropyl chloroformate. The reaction of glycidol with isocyanates produces glycidyl carbamate, which is widely used in manufacture of polyurethane foams.[28] It is used to synthesise hydraulic fluids.[29] It is also known as the stabilizer of natural oil or vinyl polymer.[30] Another important product is glycidyl methacrylate (GMA), produced industrially by reaction of methacrylic acid and glycidol, which is a dual functionality monomer ideally suited for coating and resin applications.[31]

2.3 Non-ionic surfactants

2.3.1 Surfactant definition

Surfactants are materials that lower the surface tension (or interfacial tension) between two liquids or between liquid and solid or between liquid and gas. It is typically an amphiphilic substance that exhibits a double affinity, polar-apolar duality. The reason for this is that surfactant consists of two parts (Figure 10). One is a polar group which includes heteroatoms such as O, S, P, or N, included in functional groups such as alcohol, thiol, ether, etc. The other part is an apolar group which is generally a hydrocarbon chain of the alkyl or alkylbenzene type, sometimes with halogen atoms and nonionized oxygen atoms.[32] The polar group shows a strong affinity to polar solvents, especially water, and it is usually called the hydrophilic part or hydrophile whilst the apolar part is called the hydrophobe or lipophile. Based on this, the hydrophobe portion protrudes out of the solvent surface while the hydrophilic portion remains in the solution when the amphiphilic molecule is at the interface.

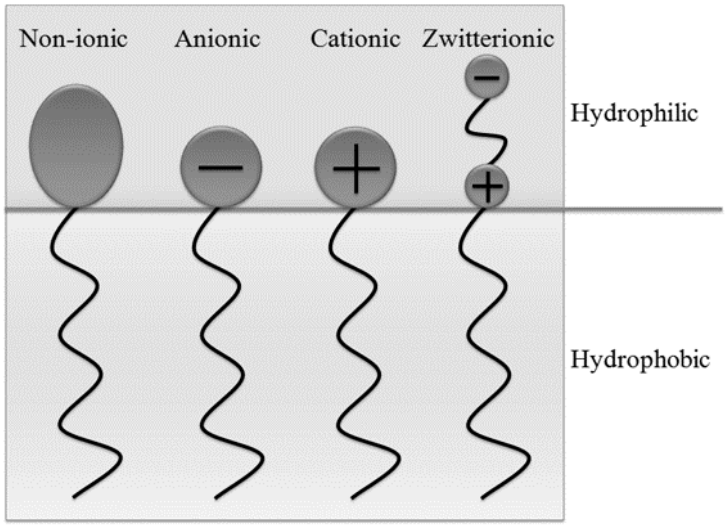


Figure 10 Molecular model of four types of surfactants[33]

When the concentration in the solvent is low, surfactants are easily adsorbed on the interface to significantly change the physical properties of the interface (the interface generally refers to the interface of liquid/liquid, solid/liquid and gas/liquid). This adsorption behavior depends on the properties of the solvent and the chemical structure of the surfactants, that is, the surfactant molecules contain both polar and non-polar groups in the molecular structure. Based on this, when the molecule is located at the interface, the lyophobic portions extend outwardly of the solvent surface and the lyophilic portions stay in the solution (Figure 11).

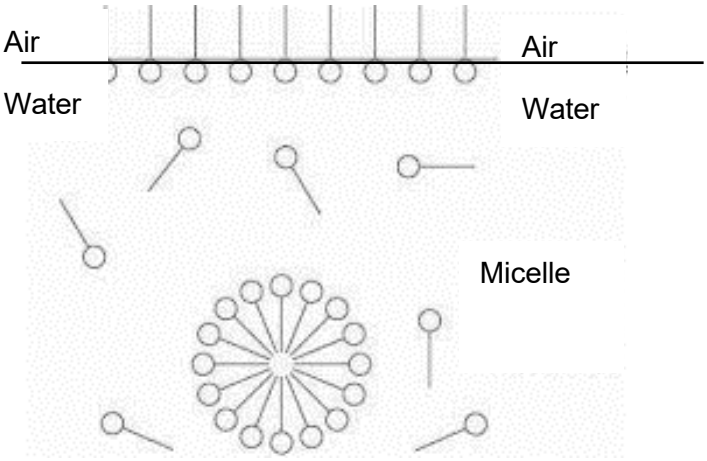


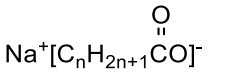
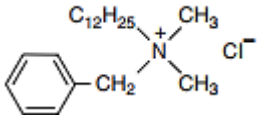
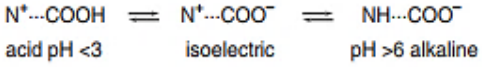
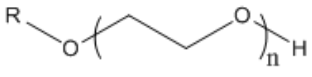
Figure 11 Surfactant Molecules in Water[34]

Adsorption is related to the change of energy because the surfactant molecules adsorbed on the interface have lower molecular free energy than the surfactants in the bulk phase. Therefore, the enrichment of the surfactant at the interface (liquid/liquid or gas/liquid) is a spontaneous process that causes a decrease in the interfacial tension. Surfactants can form monolayers directly at the interface and when its concentration in the solutions increases they form self-assembled structures (micellar vesicles, etc.). The adsorption and aggregation phenomena of surfactants are based on the hydrophobic effect, that is, the spontaneous escape of the surfactant tail groups from the aqueous phase. The reason is that the interaction between water and water is stronger than that between water and tail portion.

2.3.2 Classification of Surfactants

There are many types of surfactants and the classification methods are also different, such as ion type, solubility, application function, structure and so on. But usually according to the surfactant molecules ionizable or not in aqueous solution, they are divided into two types, ionic and non-ionic surfactants. According to the different ion of surfactants, ionic surfactants can be divided into anionic, cationic and zwitterionic surfactants.[35] Table 1 shows some examples of each type of surfactants.

Table 1 Molecule structure examples of four types of surfactants

Surfactant Type	Molecule structure example
Anionic surfactants	
Cationic surfactants	
Amphoteric surfactants	
Non-ionic surfactants	

a. Anionic surfactants

Anionic surfactants are the most developed and the most widely used surfactants with the largest production and varieties. Its molecules are generally composed of long chain hydrocarbon (C10 ~ C20) and hydrophilic groups (carboxylic acid group, sulfonate group, sulfate group or phosphate group). One of the largest yield and most widely used is the anionic surfactant whose hydrophilic portion is sulfonate, followed by sulfate (ester). Anionic surfactants have excellent detergency, foaming, wetting, dispersing and emulsifying properties, so they are widely used as detergents, wetting agents, emulsifiers, foaming agents and solubilizers, for example, sodium alcohol ether sulphate usually used as textile industry wetting agent and cleaning agent.[36]

b. Cationic surfactants

The hydrophilic end of cationic surfactants contains a positively-charged ion, or cation. Compared with various types of surfactants, cationic surfactants are most effective in regulating and bactericidal effect, despite the disadvantages of poor detergency, foaming, compatibility and high price. Cationic surfactants are used as additive

surfactants in liquid detergents, generally used in higher grade products, mainly for shampoos and it cannot be replaced by other types of surfactants in this term. The common cationic surfactants are cetyl dimethyl ammonium chloride, octadecyl trimethyl ammonium chloride, cationic guar gum (C-14S), cationic panthenol, cationic Silicone oil, dodecyl dimethyl amine oxide (OB-2) and so on. Used as fabric softener, paint ink printing auxiliaries, antistatic agents, fungicides, asphalt emulsifiers, conditioner. Because of the surface of the general substrate carrying negative ions, when the positively charged cationic surfactants contact with them, the dirt on surface will be combined, not to be dissolved so generally they cannot be detergent independent, for example, amine salts cationic surfactants used for fiber softeners.[36]

c. Amphoteric surfactants

Amphoteric (zwitterionic) surfactants are compounds containing both cationic and anionic groups, and according to the chemical structure, it can be divided into: betaine type, amino acid type, phosphate type, imidazoline type and other such as polymers, heteroatoms and other amphoteric surfactants. Amphoteric surfactants stand out because of its unique versatility: (a) low toxicity and low irritation to the skin, eyes; (b) that it can be used in hard water or high concentration of electrolyte, even in seawater; (c) good biodegradability; (d) excellent antistatic properties; (e) good bactericidal, antifungal and emulsifying ability; (f) that it can be adsorbed on the surface of a negatively charged or positively charged material without generating a hydrophobic layer which means good wetting and foaming ability. Amphoteric surfactants are generally quite expensive and therefore their use is limited to very specific applications such as cosmetics as well as safety foaming agents for hair shampoo, fiber detergents and fungicides. For example, alkyl glycines can be used as a fungicide and quaternized fatty amide glycines can be used in infant shampoo for its mild property and low irritation.[36]

d. Non-ionic surfactants

Non-ionic surfactants (NIS) are the second most important surfactants, accounting for about 45% of the total industrial production.[37] They are not ionized in aqueous solutions because their hydrophilic groups are not separable, such as alcohols, phenols, ethers, esters or amides. Most of these non-ionic surfactants are polyethylene glycols obtained by polycondensation of ethylene oxide, known as polyethoxylated non-ionic surfactants. In the case of lipophilic groups, it is often the alkyl or alkylbenzene type, the former obtained from fatty acids of natural origin. It has good performance of solubilization, washing, antistatic and low irritation. The lipophilic group in its molecule is often eight to eighteen carbon hydrocarbon chain and the hydrophilic group is often hydroxyl or polyoxyethylene. Non-ionic surfactants are soluble in water or organic solvents such as dimethylformamide (DMF) in an electrically neutral or micellar state. They are stable in acidic, alkaline and neutral electrolyte solution and can be used in conjunction with other surfactants. According to the hydrophilic group, NIS are mainly divided into three types of polyoxyethylene type, polyol type and nitrogen type. Non-ionic surfactants have a cloud point effect[38] and lower critical micelle concentration (CMC) than other types surfactants. Their Hydrophilic-lipophilic balance (HLB value) is controllable, that means, its interface properties can be tailored for a specific purpose or application.[39] They are widely used in pharmaceutical research, often used as a dispersant, emulsifier and suspension.

2.3.3 Surfactant properties

The most important properties in industry application of surfactants are wettability and permeability, emulsification and demulsification, dispersibility, solubilization, foaming and defoaming and detergency. The other relevant properties are: flexibility, antistatic, bactericidal and anti-corrosion ability.

There are four key parameters that are characteristic of every surfactant that basically describe its physical and chemical properties, and those are critical micelle

concentration (CMC), cloud point, foaming ability and solubilization, which can determine their use and application.[40]

2.3.3.1 Critical micelle concentration (CMC)

Critical micelle concentration (CMC) is the concentration of surfactant above which micelles form. At low concentration, most surfactant molecules align at the surface of air/water interface. When more surfactant is added, the surface tension of the solution starts to rapidly decrease because of the enrichment of surfactant molecules at the surface. When the surface becomes saturated, addition of more surfactant will cause formation of micelles. This concentration point (of surfactant) is what is known as critical micelle concentration (Figure 12).

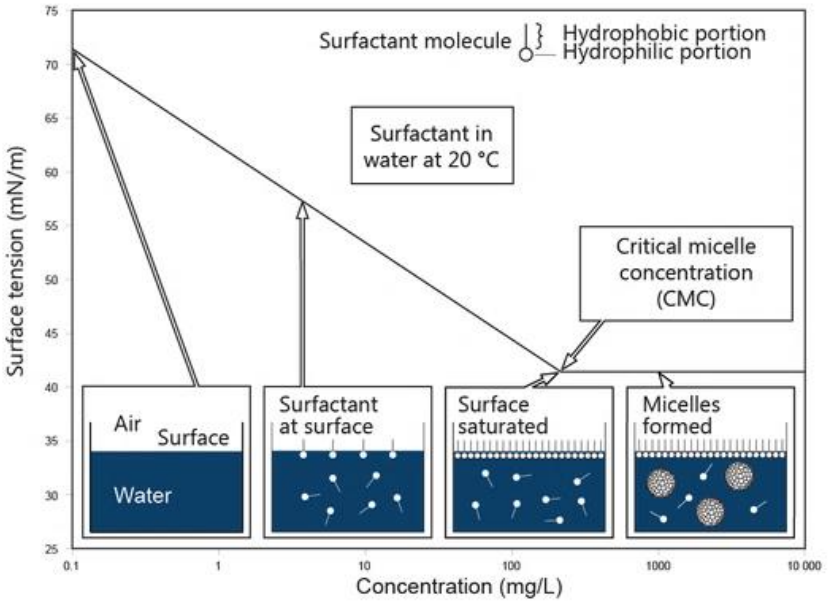


Figure 12 Surface tension against the surfactant concentration[41]

CMC values provide a useful guideline to compare surfactant detergency. Other components in solution and temperature also have big influence on micelle formation.

Therefore, finding a simple and convenient measurement method for CMC test is very important in practical applications. Since the physicochemical properties of solutions

do not change when the concentration is above CMC, such as surface tension, electrical conductivity, turbidity, osmotic pressure, density, viscosity, and light scattering, many different methods have been researched to CMC tests. These include spectrophotometry, colorimetric, potentiometry, refractometry, conductometry, capillary electrophoresis, light scattering, and so on.[42] The most common method is surface tension measurement. Two classic techniques for surface tension / interfacial tensiometry which are the Wilhelmy plate method and DuNouy ring method.

There are many variants of the Wilhelmy plate methods but all are based on balancing the static forces of surface tension, gravity, and buoyancy acting on a thin plate (usually made of glass or platinum) suspended vertically at the air-liquid interface (Figure 13).[43]

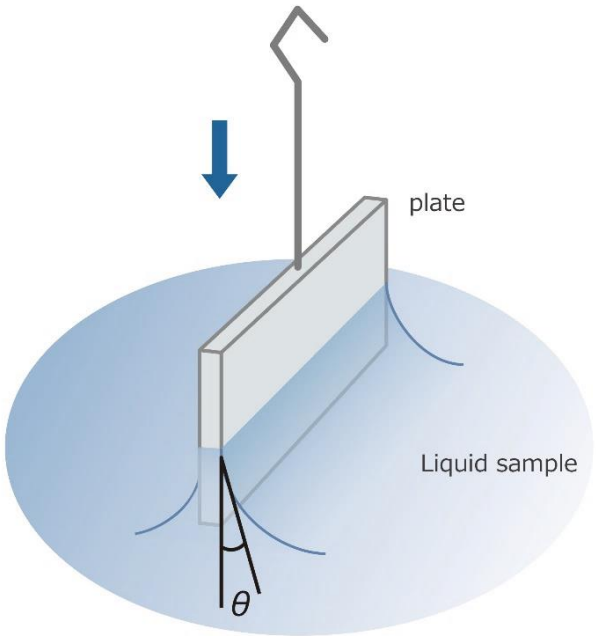


Figure 13 Illustration of Wilhelmy plate method[44]

The surface tension γ is then determined from:

Equation 1

$$\gamma = \frac{F}{L\cos\theta}$$

where, F is the measuring force (force acting on the plate), L is the perimeter of plate, θ is the contact angle of plate and the liquid. Since the board does not move during the measurement, the Wilhelmy plate method allows precise determination of surface kinetics over a wide range of time scales and it has low operator errors.

The DuNouy ring method as shown in Figure 14 is another technique by which the surface tension of a liquid can be measured. The method involves slowly lifting a ring, often made of platinum, from the surface of a liquid. The force, F, required to raise the ring from the liquid's surface is measured and related to the liquid's surface tension, γ:

Equation 2

$$F = 2\pi(\tau_i + \tau_a)\gamma$$

where τ_i is the radius of the inner ring of the liquid film pulled and τ_a is the radius of the outer ring of the liquid film.[45]

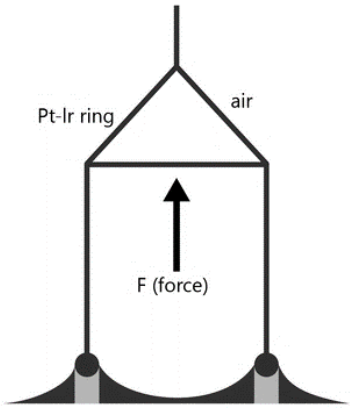


Figure 14 Schematic diagram of the DuNouy ring method

The method chosen in my research is called sessile drop method where small gas bubbles or liquid droplets are spherical but deform, under the action of gravity. The surface area of a sphere is proportional to its squared radius and the gravitational deformation depends on its volume which is proportional to the radius raised to the

third power. If the effects of surface and gravitational forces are comparable, then the surface tension of the liquid (or interfacial liquid/liquid) can be calculated from the droplet or bubble shape.

In automated apparatus, a computer program analyses the droplet or bubble shapes and calculates the surface tension of the liquid from these images (Figure 15). Surface tensions (liquid/air) as a function of concentration in dilute aqueous solution is recorded using a drop shape analysis tensiometer in pendant drop mode. A plastic syringe with a flat tip needle is used to create the drops. Photographs of the drops when they approach to the rupture point were taken and their geometry were optically analyzed by computer to give an interfacial tension value. As the surface tension and log concentration is in linear relationship when the concentration is lower than CMC, the CMC as a turning point in the relational graph is easy to find.

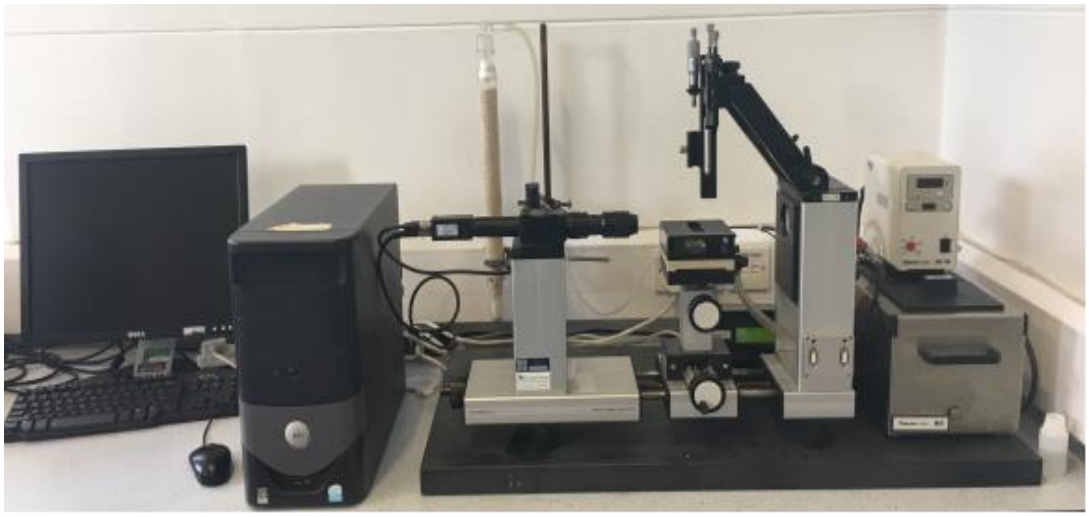


Figure 15 Contact angle tensiometer system used for CMC determination

As discussed above, there are many new techniques to measure CMC of surfactants such as pyrene fluorescence probe spectroscopy.[46] Among the reported methods, fluorescence probe technique has attracted much attention owing to its simplicity, sensitivity, ease of operation and low cost.[47] Fluorescent method for CMC tests is based on the fluorescence properties of different probes in solutions with these micelles.

2.3.3.2 Surface adsorption

The surface activity of a surfactant is derived from the amphiphilic structure of its molecule. Surfactants are enriched at the interface of oil/water or air/water as a monolayer. When the surface reaches saturation, the surfactant molecules cannot be enriched on the surface, and the hydrophobic interaction of the hydrophobic group is forcing molecules to escape the water phase. The surfactant molecules inside the solution will take another way to keep away from water, with the hydrophilic head regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle centre.

In order to demonstrate the surface activity, the following equation presents the effect of reduced surface tension $\Pi_{\mathrm{cmc}}\ (\mathrm{mN}\cdot\mathrm{m}^{-1})$

Equation 3

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc}$$

wherein, γ_0 ($mN\cdot m^{-1}$) is the surface tension of water; γ_{cmc} ($mN\cdot m^{-1}$) is the surface tension of NIS aqueous solutions whose concentration is higher than CMC. γ_0 ($mN\cdot m^{-1}$) is presents by Harkins method:[48]

Equation 4

$$\gamma_0 = 75.796 - 0.145\mathrm{t} - 0.00024\mathrm{t}^2$$

Here, t is centigrade degree and this equation is suitable for the temperature range of 10 °C - 60 °C. For the pure liquid, the effects of temperature on pressure are analyzed in two aspects. The first one is the effect on liquid molecules interact with each other from temperature that with the temperature increasing, molecular thermal motion rises accompanied by molecular kinetic energy up, leading to the energy reduction from

the internal to the surface of liquid molecules. The second one is that at the macroscopic level, the surface tension decreases as the temperature increases.

The experimental study of the relationship between surface tension and gas pressure is not easy to understand and is complex. In general, on increasing the pressure of a system, the adsorption of gas on the liquid surface and the solubility in the liquid increases so that surface tension decreases.

As described above, the decrease of surface tension is due to the fact that the NIS is adsorbed at the air/water interface. Two parameters, the maximum surface excess concentration, Γ_{max} (μmol/m^2) and the minimum area per surfactant molecule A_{min} (m^2/μmol), are used to compare the adsorption of each surfactant molecule at the air-water interface. According to Gibbs adsorption equation, these two parameters can be calculated as follows:

Equation 5

$$\Gamma_{max} = -\frac{1}{RT}\left(\frac{d\gamma}{dlnc}\right)$$

Where c (mol/l) is surfactant concentration with which the concentration of interfacial solute substance varies; *R* represents gas constant; T represents absolute temperature (K); γ_{cmc} (mN·m^{-1}) is surface tension; and dγ/d(lnc) means the slope of the γ versus lnc dependency when concentration is close to CMC.

A_{min} can be calculated according to the following equation (Equation 6):

Equation 6

$$A_{min} = \frac{1}{N_A \Gamma_{max}}(\times 10^{23})$$

In this equation, N_A represents Avogadro number.

2.3.3.3 Hydrophile-lipophile balance (HLB)

The hydrophile-lipophile balance (HLB) is another significant property of surfactants which describes the water-solublility, showing the relationship of the hydrophilic and hydrophobic groups of a surfactant, come up by Griffin in 1949[49] and 1954.[50] Griffin's method to calculate HLB of non-ionic surfactants was described in 1954 and works as follows:

Equation 7

$$\mathrm{HLB} = 20 \times M_h/\mathrm{M}$$

M_h-----the molecular mass of the hydrophilic portion of the molecule;

M----- the molecular mass of the whole molecule.

In some researches, HLB values calculated from Griffin's method did not match the experimental results, and with technology developed, HLB values of some new surfactants are more than 20. In 1957, Davies[51] claimed a method which calculates the value of both stronger and weaker hydrophilic groups of the molecule:

Equation 8

$$HLB = 7 + \sum_{i=1}^{m} H_i - n \times 0.475$$

where:

m - Number of hydrophilic groups in the molecule;

H_i - Value of the i hydrophilic groups;

n - Number of lipophilic groups in the molecule.

The HLB system is particularly useful to identify surfactants for industrial use. There are two basic emulsion types: water-in-oil emulsions (w/o) require low HLB (3-6)

surfactants, and oil-in-water (o/w) emulsions often require higher HLB (8-16) surfactants. When HLB is lower than 3, the surfactant is applied to antifoaming agents while when the HLB is higher than 15, the surfactant can be used as solubilizing agents.[51]

2.3.3.4 Cloud point (CP)

When an aqueous surfactant solution is heated, the solution will become turbid at a certain temperature, which is called the cloud point temperature. After phase separation, one phase is surfactant-enriched and the other phase contains lower concentration of surfactant (the micelle concentration is greater than or equal to CMC). The hydrophobic substances solubilized in the micelles enter the condensed phase with the micelles, and the hydrophilic substances remain in the aqueous phase, enabling separation.

The addition of salts (such as chlorides or sulfates) to the non-ionic surfactant solution leads to the hydrogen bonds in the micelles to be disrupted to reduce the cloud point temperature, for example, adding 0.1 mol/l Na_2SO_4 to the non-ionic surfactant $C_{12}EO_{10}$ aqueous solution can reduce its cloud point from 86.0 °C (1% Aq soln) to 80 °C.[52] Schott found that Na^+, K^+, Cs^+, Rb^+, and NH^+_4 can compete with polar groups of NIS for water molecules, so they can reduce cloud point while other cations can increase the cloud point, due to the complexation of them.[53] Adding organic substances such as fatty alcohols, fatty acids, phenol and urea also increases cloud point.[54] However, only high concentration (over 0.01 mol/l) of electrolyte can change cloud point apparently, otherwise, the influence on cloud point is little. Ionic surfactants are rarely used for cloud point extraction alone because of their high concentration of critical micelles and low separation efficiency.[55]

The process based on cloud point phenomenon to separate the hydrophilic substances and hydrophobic substances is named cloud point extraction. Non-ionic

surfactants are widely used in this technique. Cloud point extraction is a new type of separation technology developed in recent years, mainly using the surfactant solution solubilization and phase separation to achieve solute enrichment and separation.[56] Compared to conventional liquid-liquid extraction processes, cloud point extraction does not require the use of a large amount of organic solvent and is easier to operate, friendlier to the environment and low cost. [57] It can also protect the original properties of the extracted material (such as the biological macromolecule activity), while providing a high enrichment rate and extraction rate, so it is a new separation method and extraction technique for the potential industrial applications and the potential alternative to organic solvents. Although initially proposed as a method of enriching metal ions with hydrophobic complexes, now it has been extensively applied to other areas.

2.3.3.5 Foaming ability

Foam is the dispersion of the gas in a liquid, in which the gas is the dispersed phase and the liquid is as dispersion medium. Foam is a thermodynamically unstable system and the reason for this instability is that the system has a large interface area and a high surface energy, so the system has a spontaneous tendency to reduce the interface area to minimize its energy. Pure liquids cannot form bubbles unless a surfactant is present.

The formation of foam takes place mainly because of the adsorption of the surfactant in the solution, which is due to the decrease of surface tension between gas and liquid. Generally anionic surfactants have better foaming and foam stability than non-ionic surfactants because they have electric charge to interact with water.[58]

The foam manufactured from beer, champagne, soapy water or aqueous solution is called liquid foam; cake, bread and other elastic substances, also biscuits, foam cement, foam plastic and foam glass are solid foam. [58] In the liquid foam, the interface

between the liquid and the gas plays an important role. The foam formed from the liquid and the gas has two phases.

According to the Gibbs adsorption formula,[59] the surfactant in the solution is adsorbed on the gas-liquid interface during the formation of the foam. The interface between the liquid bubble is called Plateau border, as shown in Figure 16 at the P point. According to the Laplace potential theory, the pressure at point P in the solution is less than the pressure at point A, so the liquid flows spontaneously from A to P, leading to that the liquid film is gradually thinned. This process is called the foam drainage process. When the liquid film thinned to a certain extent, it will lead to liquid film rupture and foam damage.

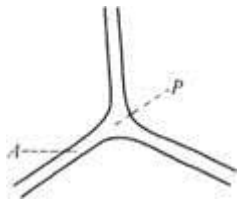


Figure 16 Boundary of foam

For instance, if a dilute aqueous solution of butanol and another of saponin were placed separately in the test tubes and shaken, then the former one produced a large number of foam while the later one formed little. However, the foam of butanol aqueous solution would disappear soon but foam of saponin aqueous solution would remain for a significant period of time. Thus, it is hard to determine which solution has a good foaming ability because the standards for both foaming and foam stability are different. The foam ability is judged by the amount of foam produced by shaking or stirring under certain conditions. Some anionic surfactants, such as sodium fatty acid, sodium alkyl benzene sulfonate and sodium alkyl sulfate have good foaming ability, and they are good foaming agents.[60]

The Ross-Miles method is popular method for evaluating the foam forming stability of a surfactant solution based on the measurement height. It is named after the founders,

John Ross and Gilbert D. Miles.[61] Some international standards deviate from this approach, where ASTM D1173[62] is the closest to the original publication and the most widely used method. The foaming solution is placed in a very high cylindrical container with standard dimensions (Figure 17). Above this container, another amount of the same solution is also contained in the normalized container. The upper solution passes through the cylinder and is mixed with the receiving phase under turbulence to produce foam. The foam height is measured as soon as the reservoir is empty and also after one, three and five minutes.

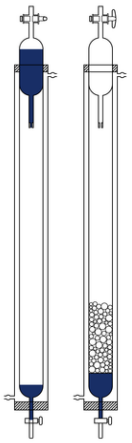


Figure 17 Diagram of the Ross-Miles method[61]

Despite this, the foamability of the surfactants synthesized here has been determined using a less accurate but reasonably effective method named “cylinder shake test”, using a graduated cylinder to record the different foam volume of same volume samples.[63] The operation is simpler and the results are more intuitive than other types. Also, Ross-Miles method needs expensive equipment which would lead to high cost.

2.3.3.6 Solubilization

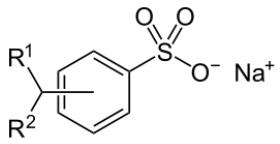
Solubilization is a phenomenon that the solubility of insoluble organic compounds is greatly increased when the concentration of the surfactant in the aqueous solution reaches the critical micelle concentration. Surfactants can have this property after

micelles are formed. The solubilization capacity is often expressed in terms of solubilizing amount (amount of solubilized organic substance per mole of surfactant in grams). The value of solubilization is related to the structural characteristics of surfactants, solute, temperature and other factors. In terms of solubilization, the molecules with saturated hydrocarbon chains are stronger than the one with unsaturated hydrocarbon chains and solubilization of non-ionic surfactants is generally more obvious than other types. This property plays an important role in emulsion polymerization, micellar flooding, washing and some physiological processes.[64]

2.3.4 Non-ionic surfactants

2.3.4.1 History and development of non-ionic surfactants

The world produces about 18 million tons of soap, detergents and other surfactants in 1970, 25 million tons in 1990 and 40 million tons in 2000.[65] In 1940, the production of surfactants mainly consisted of soap (fatty acids), manufactured with a very old technology. At the end of the Second World War, short-chain olefins were popular in the petroleum refining market, especially C2-C3 from catalytic cracking. In the early 1950s, propylene was not used for any purpose while ethylene was used in the manufacture of styrene. The low cost and polymerization possibilities of propylene to transfer into C9-C12-C15 hydrophobic groups, made it an inexpensive alternative to alkyl groups derived from natural or synthetic fatty acids.[66] The alkylbenzene synthetic detergent alkylbenzene sulfonate (ABS) (Figure 18) was born, and they soon replaced the fatty acid soaps for their use in washing machines.[67]



$R^1 + R^2 = C_{11}H_{24}$

Figure 18 Molecular structure of sodium dodecylbenzenesulfonate

The environmental protection laws were passed around 1965 of restricting and prohibited the use of propylene-based alkylate in the United States and Europe.[68] Surfactant manufacturers have had to find new raw materials and methods to produce linear alkylates, such as ethylene polymerization and molecular sieve extraction. This situation is conducive to the developments of different types of surfactants, leading to a wide range of products at present.

In the 1960s, steam cracking developed rapidly with mainly production of ethylene, that also contributed to the low cost of ethylene oxide production, which is the basic raw material of non-ionic surfactants. In the 1970s, new formulations were proposed to make the use of surfactants not only for domestic but also for industry. In 1980-1990, the production of non-ionic surfactants grew faster than that of anionic types, especially with the introduction of new non-ionic surfactants, such as alkyl polyglucosides.[69]

2.3.4.2 Types of non-ionic surfactants

When non-ionic surfactants are dissolved in water, their hydrophilic groups (e.g.-OH, -O-, -NH_2) do not dissociate. Non-ionic surfactants are mainly divided into three categories: polyoxyethylene and its derivatives, polyol and fatty acid esters and nitrogenated non-ionic surfactants.[70] Non-ionic surfactants are now used in large kinds of domestic and industrial products, for example, powdered or liquid formulations. However, the most significant in market is polyethoxylated products (Table 2), especially used in household detergents.[71]

Table 2 Main Non-ionic Surfactants and Portion of Market

Surfactant Type	Percent of Market (%)
Ethoxylated Linear Alcohols	40
Ethoxylated Alkyl Phenols	15
Fatty Acid Esters	20
Amine and Amide derivatives	10
Alkylpolyglucosides	With other types 15%
Ethyleneoxide/Propyleneoxide Copolymers	
Polyalcohols and ethoxylated polyalcohols	
Thiols (mercaptans) and derivatives	

a. Polyoxyethylene non-ionic surfactants

The polyoxyethylene surfactants are made by addition reaction of a compound containing a lipophilic group and active hydrogen atoms with ethylene oxide. Any compounds containing functional groups such as -OH, -COOH, $-NH_2$, $-CONH_2$ and so on are easily reacted with ethylene oxide to form a polyoxyethylene surfactant with catalyst.

At present, compounds containing active hydrogens that commonly used in industry are: fatty alcohols, alkyl phenols, fatty acids, fatty amines and fatty amides, sorbitol and sucrose. The more number of ethylene oxide units is in a surfactant molecule, the more water-soluble a surfactant will be.

b. Polyol non-ionic surfactants

Polyhydric alcohol surfactants are esters or amide compounds derived from polyhydric alcohols, alkyl alcohol amines or sugars containing multiple hydroxyl

groups, reacted with higher fatty acids, especially ethylene glycol, pentaerythritol glycerol, sorbitan and sucrose. In the molecule, lipophilic groups and hydrophilic groups are linked by the ester bonds, and it is prone to get hydrolysis reaction. If the ester bond is replaced by amide, it is not easy to hydrolyze and is more stable. Alkyl glycosides are derivatives with acetal structure manufactured from a hemiacetal hydroxyl group of sugar with alcohol. Alkyl polyglycosides not only have high surface activity, good detergency and compatibility, but also are non-toxic, non-stimulating and fast-biodegradable, so that alkyl polyglycoside can be used in cosmetics.

c. Nitrogen-containing non-ionic surfactants

This type of surfactant includes alkyl alcohol amides, amine oxides, block polyethers and sterol derived non-ionic surfactants. Alkyl alcohol amide is commonly made by fatty acid with ethanol amine after condensation in the system. Amine oxide is a polar non-ionic surfactant and depending on the different pH of the solution, the amine oxide can show non-ionic properties or strong ionic properties. Block polyether is the block copolymer non-ionic surfactants based on ethylene oxide, propylene oxide or other olefin oxide as the main body, with some active hydrogen compounds as the initiator. Tests show that sterol surfactants present low toxicity and can be used in the pharmaceutical field, such as that phytosterols are particularly effective in lowering serum cholesterol levels.[72]

2.3.4.3 Fatty acid Esters

The esterification of fatty acid by -OH groups from polyethyleneoxide chain or polyalcohols produces an important series of non-ionic surfactants. Their market share is 20% of all non-ionic surfactants and their outstanding compatibility with biological tissues makes them in pharmaceuticals, cosmetics and food industry.[73]

There are three types of fatty acid esters: acid ethoxylated fatty acids (polyethoxy-esters), glycerol esters, esters of hexitols and cyclic anhydrohexitols.

During the condensation of ethylene oxide with a carboxylic acid, Polyethoxy esters are produced as the same as esterification. Polyethoxylates of fatty acids and other natural carboxylic acids are one of the least expensive non-ionic surfactants although they cannot foam to be very good detergents. They can be used to reduce the cost of detergents, albeit limited but they cannot be used at alkaline pH, because they will hydrolyze.

Glycerol esters and their derivatives are used in foodstuffs, dairy emulsions, foams and pharmaceuticals because of their good performance as emulsifiers, dispersants and solubilizing agents. The triglycerides found in vegetable and animal oils and fats are triglycerides of glycerol (propane-triol) and cannot dissolve in water. However, in the opposite way, glycerol mono and diesters show great surfactant properties. They can be produced by the reaction of glycerol with fatty acids and by alcoholization industry.

Hexitols are hexa-hydroxy-hexanes gotten by the reduction of hexoses or monosaccharides and the most widely used type of them is sorbitol, coming from the D-glucose.[74] The molecules of this type seem to be very complex but they are readily prepared from natural raw materials, for example, fats and sugars, and it makes them widely used in food and medicine.

2.3.4.4 Fatty alcohol ethoxylate (AEO)

Fatty alcohol polyoxyethylene ether (fatty alcohol ethoxylate, AE or AEO) is a kind of non-ionic surfactant, produced by the polymerization of fatty alcohols with ethylene oxide (Figure 19). AEO is chemical stability and not susceptible to acid or metal ions. In AEO chemical structure, the more addition of ethylene oxide, the more hydrophilic molecules on the oxygen are, and the more hydrogen bonds will be able to form, the better the water solubility.

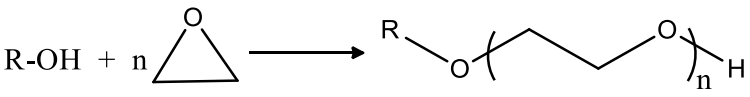


Figure 19 Synthesis method of AEO

Ethylene oxide blows through the alcohol at 180 °C and under 1-2 bar of pressure, with KOH as a catalyst.[75] The process is highly exothermic (ΔH -92 kJ/mol of ethylene oxide reacted) and careful control is required to avoid a thermal runaway.

They have already been manufactured in commercialized production and have been used in many industrial and daily products, for example, in the washing industry, textile printing and dyeing industry, paper industry and other industry such as pesticide emulsifier.

AEO3 (MOA3) can be used as a water-in-oil emulsifier, which is the main raw material for high-performance detergent fatty alcohol polyoxyethylene ether sulfate (AES). AEO7 can be used as disinfectant, degreasing agent and laundry liquid raw materials. AEO9 is mainly used for wool lotion, wool industrial degreasing agent, fabric detergent and liquid detergent active ingredients, general industrial used as emulsifier.[76]

According to different requirements, AEO can be widely used in emulsification, wetting, dyeing, spread, washing and many other industries by connected to 1 ~ 30 moles of ethylene oxide. They have excellent biodegradability and low temperature performance, and would not be affected by water hardness. They are more suitable for washing synthetic fiber and can be used for powder formulations, also for liquid detergent formulations.

2.4 Synthesis methods of non-ionic surfactants

2.4.1 Methods of Glycerol Ether synthesis

Nowadays, surfactants are produced mainly from fossil-based raw materials. However, facing serious environmental forms, it raises a growing demand for sustainable surfactants with lower cost but great performance. One possible solution is to use glycerol as an alternative to replace ethylene oxide to produce non-ionic surfactants, which can achieve 100% biobased products when combined with alkyl chains from bio-based sources.

In the early years, the study of synthesis of glycerol ethers was focused on modifying the hydrophilic and hydrophobic parts, in order to develop different types of compounds with outstanding biological and physical properties.[77] Polyethylene glycols(PEGs), as a classic non- ionic surfactant, are usually made from Ethylene glycol(EG) by addition reaction with ethylene oxide.[78]

2.4.2 From Glycerol

Glycerol is the most common and available material to produce non-ionic surfactants. In fact, the glycerol monoesters and diglycerides prepared by transesterification of triglycerides with excess glycerol in the present of basic catalysts are the main glycerol-based surfactants on the market. However, its application is limited since the poor hydrolysis stability of the ester bonds. Therefore, alkyl polyglycidyl ethers obtained from glycerol and hydrophobic carbon chains (≥8 carbon atoms) are considered to be non-ionic surfactants with higher solubilization and emulsifying ability than alkoxylates. Unfortunately, the direct etherification of glycerol or polyglycerol with long alkyl chains (≥8 carbon atoms) is still a challenge today because of the low reactivity and poor selectivity.[79]

The direct etherification of glycerol and fatty alcohol also attracts a lot of attention due to the low price of reactants. In this case, most of reported studies take direct etherification of glycerol with active or light alcohols into account.[80] Little attention has been made to the direct etherification of glycerol with long-chain aliphatic alcohols.[81] The Weckhuysen group have reported direct etherification of polyols and long-chain olefins with heterogeneous acidic catalysis, in which diols can be converted in high yield.[82] However, low conversion (about 20%) was reported with the triol, glycerol.[83,84] Glycerol has difficulties in interacting with hydrophobic substances because of its high viscosity and hydrophilicity, leading to miscibility problems. In addition, low selectivities are likely because glycerol can also give homo- and hetero- etherification products because of its multiple hydroxyl groups.

The Lemaire group prepared glycerol ethers from glycerol in the presence of Pd/C as catalyst and camphorsulfonic acid as a co-catalyst, but the yield was low when reacting with long alkyl chain alcohols (41% and lower).[85] In 2015, SOLVAY reported the synthesis based on the direct etherification of glycerol and dodecanol with co-polymer of polystyrene (PSt) and polystyrene sulfonic acid (PSSA) as shown in Figure 20. However, due to the large number of by-product ethers, including di-fatty alcohol ethers and polyglycerols, the selectivity to monoalkyl glycerol ethers is low and the maximum conversion of dodecanol is 60%.[86]

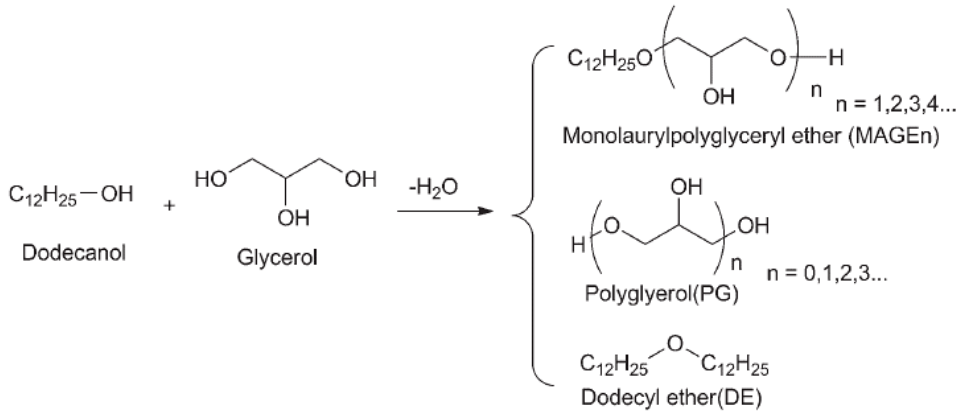


Figure 20 Etherification of glyerol and dodecanol (SOLVAY)[71]

Therefore, some alternatives to glycerol such as ketals[87] and epichlorohydrin[88] have been used and satisfactory yields have been obtained from reactions with alcohols. However, these can create environmental and safety issues because these reactive glycerol derivatives are toxic and also lead to the generation of salts in the reactions.

2.4.3 From EP

A cleaner synthetic route to glyceryl ether biosurfactants is through ring-opening of glycidol by the fatty alcohol (Figure 21). This route has been patented by L'air Liquide [US2011/0009676][89] of the production of 1-alkyl glycerol ethers for use in cosmetic, pharmaceutical and household products.

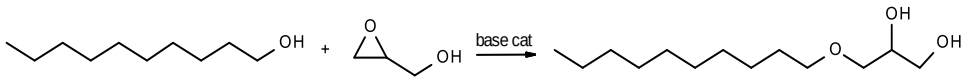


Figure 21 Etherification of glycidol and fatty alcohol giving non-ionic surfactant

The most common way is as follows. Glycidol is dropped into the obtained reaction product which comes from the reaction of alcohol with base catalyst, to react with the alcohol.[90] However, this method gives rise to frequent problems, such as low

conversion rate of the alcohol and large burden of purification to remove the unreacted alcohol. Catalysis was the main technological tool to obtain efficient and selective alkylation or arylation. The use of Bronsted or Lewis acids in solution for catalysis on organic, inorganic or hybrid materials has been extensively tested.[91]

Akira Saito working for KAO corporation improved this route by reacting an alcohol with glycidol in the presence of the simple metal salt of rare earth element ($M(OSO_2R^2)_x$) as a catalyst. Then they found the conversion of the alcohol is about 55% and EP 99%.[92]

2.4.4 From GLC

Glycerol carbonate can also react with alcohols to give alkyl glyceryl ethers. In the reaction between GLC and alcohol, the kinetic product is the formation of carbonate bond, however this is a reversible equilibrium reaction. Over time, the alkyl glyceryl ether accumulates, which is irreversible. As glycerol carbonates are more readily available than glycidol in derivatization chemistry involving alcohol etherification. This can significantly reduce the cost of raw materials.

Rhodia operations published a process of preparing glycerol ether from glycerol carbonate in the presence of a base (such as KOH). However, this method cannot provide good yields of glycerol ether because it is mostly transformed to transcarbonation.[93]

In the patent of WO 2013139995 A1, GLC was reacted one hour with linear alcohol (molar ratio 1:4) in the condition of 140°C, nitrogen air and condenser pipe existing in presence of solid acid Amberlyst 35. After extraction of water and CH_2Cl_2, evaporation under reduced pressure and purification by chromatography on flash silica column, the final yield is all under 50% with conversion over 85% (Figure 22).[94]

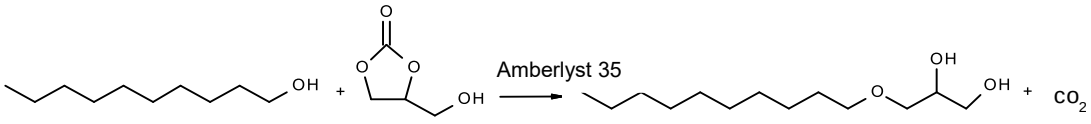


Figure 22 Etherification of glycerol carbonate and fatty alcohol to yield non-ionic surfactant and CO_2

2.4.5 Methods of poly phenol ethoxylate synthesis

In the alkylphenol ethoxylates (APEO), nonylphenol polyoxyethylene ether takes maximum proportion, accounting for more than 80%. As phenol is weak acid and the degree of its acidity is greater than the fatty alcohol, so the generation of adducts is speedier and the product does not contain free phenol.

There are two methods in generally manufacture. (1) Direct alkane chlorination generates an haloalkane then has condensation with phenol in the present of Lewis acid. (2) Olefins directly react with phenol in the present of Lewis acid.[95]

As nonylphenol ethoxylate is the most important category of alkylphenol ethoxylates. The most common material used for synthesis is ethylene oxide. The Dow Chemical Company uses the method that nonylphenol ethoxylates are prepared by reacting nonylphenol and ethylene oxide with potassium hydroxide and water present. The ratio of ethylene oxide to nonylphenol determines the structure of the molecule produced (Figure 23).[96]

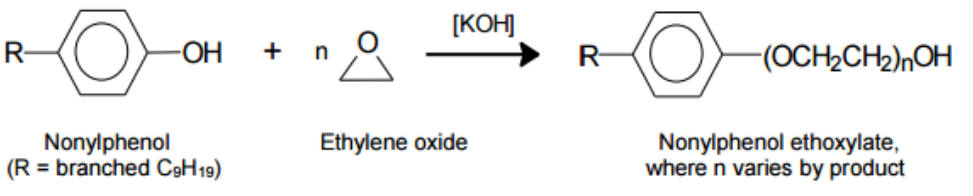


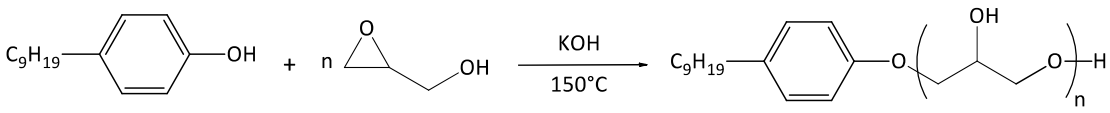
Figure 23 The reaction of nonyphenol with ethylene oxide

Kao Corporation has published another method that polyglyceryl ether derivatives are

produced from alcohol and glycidol with an aluminosilicate ion-exchanged with at ammonium ions, alkali metal ions or alkali earth metal ions as catalyst and the conversion of alcohol is about 60-70% with conversion rate of glycidol 99%.[97]

The use of strong bases is discarded in the patent above, as they claim that the moderate conversion rates as well as the removal of the large excess of alcohol makes this methodology undesired. Therefore, Lewis acid catalysts look like the most promising way to obtain poly(glyceryl) ethers.

Raymond and his group used nonylphenol and different ratio (1:3,1:6,1:10,1:12) of glycidol reacting to get alkylphenol-glycidol surfactants as emulsifiers in order to stabilize emulsions of an aqueous alkali phase and an organic phase containing a halogenated solvent (Figure 24).[98] They found that the molecular structure of product is produced according to the ratio of the addition of glycidol.



(n=3,6,10,12)

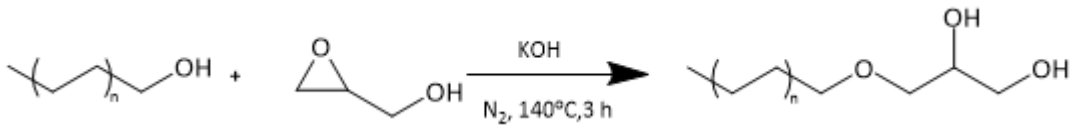
Figure 24 The reaction of nonylphenol with EP

Many reviews about potential applications of glycerol derivatives have been published recent years.[99,100] These articles show the wide interest from chemistry in this type of molecule in the field of medicine and washing products, however, only a few of them described new synthetic ways for glyceryl ether synthesis, so this technology still has a lot room for improvement.

3 Experimental work

3.1 Synthesis of alkyl glyceryl ethers from glycidol with fatty alcohols

As seen in Figure 25, alkyl glyceryl ethers are made from glycidol with fatty alcohols in this research, using potassium hydroxide as catalyst. To ensure the product formation, the molar ratio of alcohol to EP is 4:1 and EP is added dropwise using a syringe pump for three hours.



n=3 1-octanol C_8 1-o-octylglycerol

n=4 1-decanol C_{10} 1-o-decylglycerol

n=5 1-dodecanol C_{12} 1-o-dodecylglycerol

n=6 1-tetradecanol C_{14} 1-o-tetracylglycerol

n=7 1-hexadecanol C_{16} 1-*o*-hexadecylglycero

n=8 1-octadecanol C_{18} 1-o-octadecylglycerol

Figure 25 Base-catalysed synthesis of non-ionic surfactants from EP and fatty alcohols

Equipment set up includes 100 ml three neck RB flask equipped with a magnetic stirrer, a septum, a thermometer to measure the mixture temperature and a Liebig condenser, connected to an Schlenk line from the top as Figure 26. To ensure homogeneous heat to the mixture, a hot plate with a silicone oil bath is used. All the material used here are pure, no need for purification.

Figure 26 Equipment used in synthesis of alkyl glyceryl ethers

Process example of 1-o-octylglycerol:

KOH (98%, SIGMA-ALDRICH) (500 mg, 17.8 mmol) and 1-octanol (98%, SIGMA-ALDRICH) (20.83 g, 160 mmol, 25.3 ml) were added to the flask after 3 cycles of N_2-vacuum carried out. EP (>95%, GLT) (2.96 g, 40 mmol, 2.65 ml) was added dropwise using a syringe pump with a plastic syringe and a long stainless-steel needle during the reaction. The reaction was under 140°C with 800 rpm rate stirring for three hours. The mixture was then concentrated with reduced pressure distillation and the organic products were extracted three times with cyclohexane (>=99.7%, SIGMA-ALDRICH). The water added during extraction was then removed by $MgSO_4$ (Fisher Scientific UK) and cyclohexane was removed at the rotary evaporator. The excess of octanol remaining in the mixture is distilled under strong vacuum at 140°C, leaving the crude product, which is analysed by ^{1}H-NMR ($CDCl_3$ (98%, SIGMA-LDRICH), $SiMe_4$ as reference). The crude products were finally purified by silica column chromatography

(cyclohexane-ethyl acetate 3:2).

The final product is left to dry under reduced pressure for one hour to ensure complete removal of volatiles.

The experimental processes of the others synthesis of alkyl glyceryl ethers were all the same and all the material ratios used in reactions are shown in Table 3:

Table 3 The reactant material ratios used in synthesis of alkyl glyceryl ethers

Surfactant	**Alcohol amount (g)**	**Alcohol amount (mol)**	**EP amount (g)**	**EP amount (mol)**	**Catalyst**	**Cat. Amount (g)**
1-o-octylglycerol	20.87	0.16	2.96	0.04	KOH	0.5
1-o-decylglycerol	25.32	0.16	2.96	0.04	KOH	0.5
1-o-dodecylglycerol	29.81	0.16	2.96	0.04	KOH	0.5
1-o-tetradecylglycerol	34.30	0.18	2.96	0.04	KOH	0.5
1-o-hexadecylglycerol	38.79	0.21	2.96	0.04	KOH	0.5
1-o-octadecylglycerol	43.28	0.23	2.96	0.04	KOH	0.5

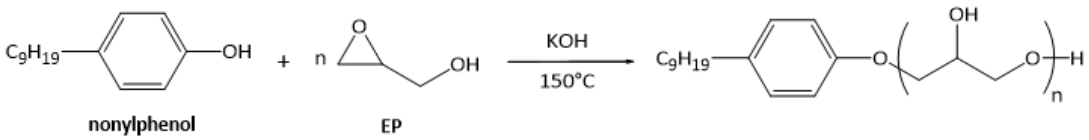
The reduced pressure distillation temperature for each product is different for the different boiling point of the alcohols. For 1-octanol, the temperature needs to be 95 °C, for 1-decanol it is 130 °C, for 1-dodecanol it is 140 °C, for 1-tetradecanol it is 150 °C, for 1-hexadecanol it is 150 °C, and for 1-octadecanol it is 180 °C with regular glass tubes instead of condenser because of the very high boiling point of 1-octadecanol. After the alcohol distillation, around 5 grams of orange viscous oil were obtained for

all the reactions.

3.2 Synthesis of poly(glyceryl)ether derivatives from glycidol with alcohols

Non-ionic surfactants derived from the reaction between fatty alcohols and glycidol were highly lipophilic. In order to achieve non-ionic surfactants with higher hydrophilicity, new adducts containing two or more glyceryl ether moieties were prepared.

Non-ionic surfactants C_9-Φ-G3 and C_9-Φ-G12, were synthesized by combining nonylphenol and glycidol in 3, 6, 10 and 12-fold excesses, respectively, as shown in Figure 27.



n=3, 6, 10, 12

Figure 27 Base-catalysed synthesis of surfactants C_9-Φ-G3 and C_9-Φ-G12 from EP and nonyl-phenol

Process example of C_9-Φ-G3:

Equipment: 100 ml three neck round bottomed flask in heated oil bath, magnetic stirrer, septum, and thermometer and Liebig condenser connected to a Schlenk line.

KOH (0.1 g, 3.56 mmol) and nonylphenol (ALDRICH) (10 g, 45.4 mmol) were mixed into the flask. EP (10.2 g, 137 mmol) was added dropwise using a syringe pump over five hours. After the addition, CO_2 gas was bubbled into the mixture until the pH is lower than pH 9 (~30 mins). The solution was stirred (800 rpm) at 140 °C for five hours with KOH (0.1 g, 3.56 mmol) added every hour in order to maintain the alkalinity of

the mixture. The organic product then was extracted by cyclohexane and the cyclohexane was removed at the rotary evaporator. The final product was analyzed by ^{1}H-NMR.

In order to achieve non-ionic surfactants with higher hydrophilicity from fatty alcohols, polyglyceryl ethers moieties must be synthesized. Few patents can be found in the literature, but especially relevant are two from KAO Corporation, in which they use simple metal salts of rare earth elements and aluminosilicates as Lewis acid catalysts as shown in Figure 28.[101]

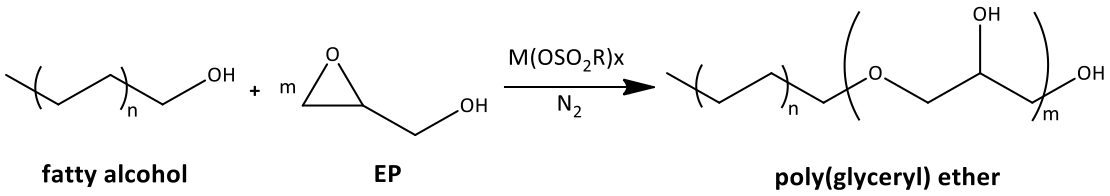


Figure 28 Synthesis of poly(glyceryl) ethers using rare earth metal salt, where n=4-8 and m=2-6

The use of strong bases is is highligheted as undesirable in both patents, as they claim that the moderate conversion rates as well as the removal of the large excess of alcohol makes this methodology undesired. Therefore, Lewis acid catalysts look like the most promising way to obtain poly(glyceryl) ethers. To verify the viability of this reaction, a very similar procedure has been carried out in the lab using lanthanum triflate, which has been proved to be very effective. Lanthanum triflate has good catalytic performance in Diels-Alder reaction, hydroxyaldehyde condensation reaction and Friedel-Crafts reaction as a water-resistant Lewis acid.[102]

Reactions to achieve surfactants C_{12}-3G and C_{12}-6G using $La(OTf)_3$ (98%, SIGMA-ALDRICH) as catalyst are processed as control experiment.

Polyglyceryl ether C_{12}-3G (Product reaction between $C_{12}OH$ and 3 eq. of EP)

Equipment: 100 ml three-neck round bottomed flask in heated oil bath, magnetic

stirrer, syringe pump, thermometer and Liebig condenser fitted with nitrogen inlet.

$La(OTf)_3$ (300 mg, 0.5 mmol) and 1-dodecanol (9.92 g, 53.2 mmol) were added to the reaction flask. EP (11.84 g, 160 mmol) was added dropwise with a plastic syringe and a long stainless-steel needle via syringe pump. The temperature of the reaction was set to 90 °C and stirred (800 rpm) for 8 hours. The conversion of glycidol is assumed to be quantitative. The resulting product is analysed by ^{1}H-NMR.

Then KOH was tested as catalyst in the same way and then was used in all the reaction because of its performance and low price as Figure 29.

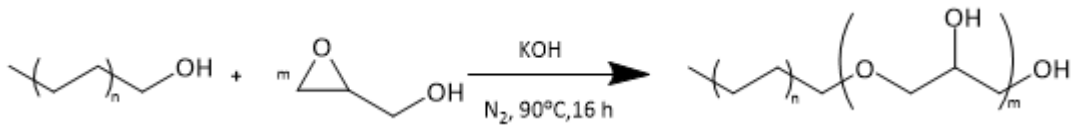


Figure 29 The base reaction of all synthesis of polyglyceryl ethers

Example：Polyglyceryl ether C_{12}-6G (Product reaction between C_{12}OH and 6 eq. of EP)

Equipment: 100 ml three-neck round bottomed flask in heated oil bath, magnetic stirrer, syringe pump, thermometer and Liebig condenser fitted with nitrogen inlet.

KOH (300 mg, 5 mmol) and 1-dodecanol (9.92 g, 53.2 mmol) were added to the reaction flask. EP (11.84 g, 160 mmol) was added dropwise with a plastic syringe and a long stainless-steel needle via syringe pump. The temperature of the reaction was set to 90 °C and stirred (800 rpm) for 8 hours. The conversion of glycidol is assumed to be quantitative. The resulting product is analysed by ^{1}H-NMR.

During all the reactions, certain ratio of alcohol and EP were added by need as in Table 4.

Table 4 Reactants ratio of polyglyceryl ethers

Surfactant C(2n+2)-mG	**FA amount (g)**	**FA amount (mol)**	**EP amount (g)**	**EP amount (mol)**	**EP:FA ratio**	**KOH amount (g)**
Surfactant C_8-2G	4.80	0.037	5.48	0.074	2	0.3
Surfactant C_8-3G	6.90	0.053	11.84	0.160	3	0.3
Surfactant C_8-4G	4.56	0.035	10.37	0.140	4	0.3
Surfactant C_8-5G	3.65	0.028	10.37	0.140	5	0.3
Surfactant C_8-6G	5.21	0.040	10.37	0.140	3	0.3
Surfactant C_8-9G	2.03	0.016	10.37	0.140	9	0.3
Surfactant C_8-12G	1.52	0.012	10.37	0.140	12	0.3
Surfactant C_{10}-3G	7.39	0.047	10.37	0.140	3	0.3
Surfactant C_{10}-4G	5.54	0.035	10.37	0.140	4	0.3
Surfactant C_{10}-5G	4.43	0.028	10.37	0.140	5	0.3
Surfactant C_{10}-6G	3.69	0.023	10.37	0.140	6	0.3
Surfactant C_{10}-9G	2.46	0.016	10.37	0.140	9	0.3
Surfactant C_{10}-12G	1.85	0.012	10.37	0.140	12	0.3
Surfactant C_{12}-3G	9.92	0.053	11.84	0.160	3	0.3

Surfactant C_{12}-6G	7.44	0.040	17.76	0.240	6	0.3
Surfactant C_{12}-9G	2.90	0.016	10.37	0.140	9	0.3
Surfactant C_{12}-12G	2.17	0.012	10.37	0.140	12	0.3
Surfactant C_{14}-3G	11.36	0.053	11.84	0.160	3	0.3
Surfactant C_{14}-6G	8.58	0.040	17.78	0.240	6	0.3
Surfactant C_{14}-9G	3.22	0.015	10.00	0.135	9	0.3
Surfactant C_{14}-12G	2.41	0.011	10.00	0.135	12	0.3
Surfactant C_{16}-6G	5.66	0.023	10.37	0.140	6	0.3
Surfactant C_{16}-9G	3.77	0.016	10.37	0.140	9	0.3
Surfactant C_{16}-12G	2.73	0.011	10.00	0.135	12	0.3
Surfactant C_{18}-9G	4.21	0.016	10.37	0.140	9	0.3
Surfactant C_{18}-12G	3.04	0.011	10.00	0.135	12	0.3

3.3 Property tests of products

3.3.1 Critical Micelle Concentration

A common procedure for determining CMC from experimental data is to find the intersection of two straight lines traced by the measurement property to the surfactant concentration curve. The most common determinants of surfactant CMC are

conductivity, surface tension, NMR chemical shift, UV-Vis absorption, self-diffusion coefficient and fluorescence intensity and surface tension is chosen to be test criteria.

Before surface tension testing, the hydrophilic – lipophilic balance (HLB) value is required to be calculated as a reference standard to determine if the whole molecule of the surfactant will be hydrophilic enough to test CMC.

In 1957, Davis proposed a method based on the calculation of molecular chemical groups. The advantage of this method is that it takes into account the effects of stronger and weak hydrophilic groups. The working principle of this method[103] is as follows:

Equation 9

$$HLB = 7 + \sum H_i - (n \times 0.475)$$

Where H_i is the assigned values of the hydrophilic groups (e.g. -O- (i=1.3), -OH (i=1.9)) and n is the number of lipophilic groups (e.g. -CH-, $-CH_2-$, $-CH_3$) in the molecule.

Table 5 and Table 6 show the group numbers of hydrophilic and lipophilic groups in HLB value calculation.

Table 5 Group number of lipophilic groups in HLB value calculation

Lipophilic Groups	Group Number
-CH-	-0.475
$-CH_2-$	-0.475
CH_3-	-0.475
=CH-	-0.475

Table 6 Group number of hydrophilic groups in HLB value calculation

Hydrophilic Groups	Group Number
$-SO_4^-Na^+$	38.7
$-COO^-K^+$	21.1
$-COO^-Na^+$	19.1
N (tertiary amine)	9.4
Ester (sorbitan ring)	6.8
Ester (free)	2.4
-COOH	2.1
Hydroxyl (free)	1.9
-O-	1.3
Hydroxyl (sorbitan ring)	0.5

In order to test the surface tension, a data physics contact angle tensiometer equipped with a camera connected to a computer has been used for surface tension measurement. Room temperature surface tensions (liquid/air) as a function of concentration in dilute aqueous solution were recorded using a drop shape analysis tensiometer (Contact Angle System OCA, Carl Stuart Ltd.) in pendant drop mode.

Interfacial tensions were measured using a drop shape analysis tensiometer (Contact Angle System OCA, Carl Stuart Ltd.) working in the pendant drop mode at room temperature (23−25 °C). Interfacial tension is derived from the fit of the pendant drop profile, and care was taken to ensure that the apparatus was calibrated with deionized ultrapure water. The drops were left to equilibrate close to the rupture point, and at least 10 consistent measurements per solution were recorded. Prior to the analysis, the samples were placed overnight in the same room where the equipment was

placed to ensure that all samples were at the same temperature.

Every sample was measured the temperature before the water droplet experiment and the temperature with syringe size were filled into the form as Figure 30.

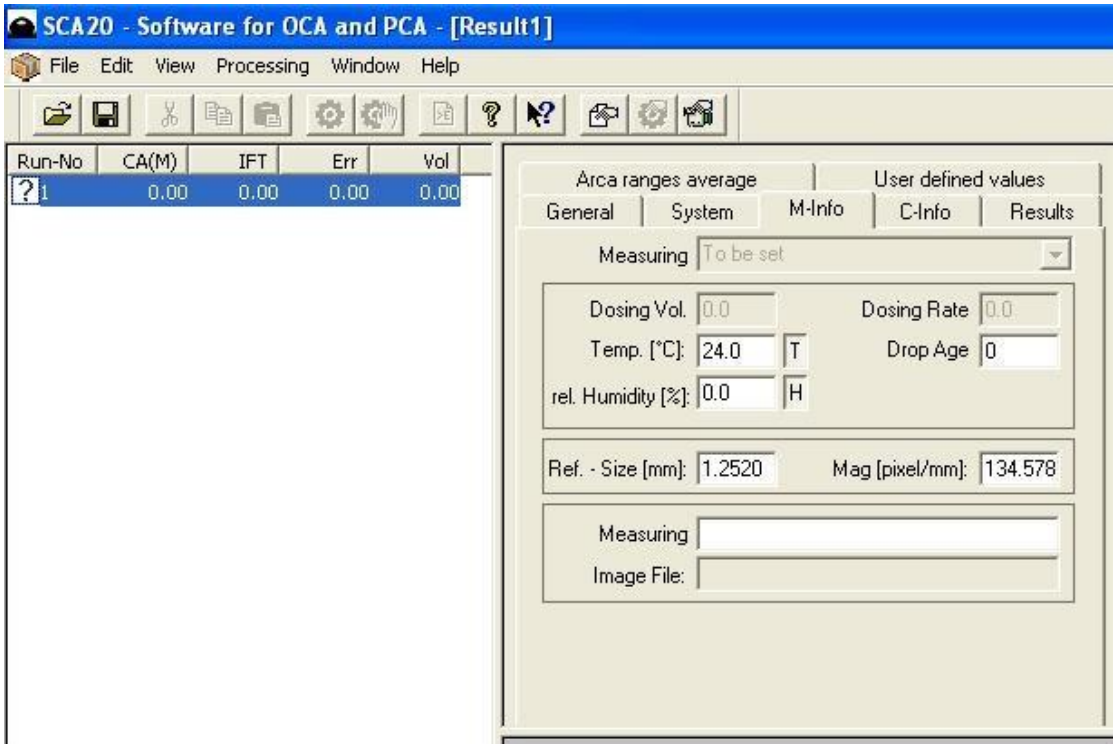


Figure 30 Enter a set value operation interface in SCA20

Before measure CMC, it is necessary to determine the measurement range. All the products were dissolved in deionized water of concentration 1g/L then tested surface tension to assume the concentration range of measurement. The measurement range of surface tension should be from 72 mN/m (water) to 25 mN/m. After determined the measurement range, every samples were prepared using pipette and deionized water. Measurements were repeated three times, and the respective mean values were taken.

3.3.2 Cloud Point

The solubility of the non-ionic surfactants in the aqueous solution decreases as the

temperature rises and becomes turbid when it rises to a certain temperature, and two liquid phases are obtained after placing or centrifuging. This temperature is called the cloud point.

As shown in Figure 31, 1 wt% aqueous solution of all the surfactants were prepared in 15 ml transparent glass bottles and were put into water bath which heated from 5 degrees to 100 Celsius degrees in 30 mins with a highly sensitive with two ends electronic thermometer in water (accuracy 0.1 °C, the average value of two ends was taken). The solution would get cloudy at a certain temperature with temperature increasing.

For the samples that could not dissolve well, they were placed in the ultrasonic shaker for 24 hours.

Figure 31 Equipment used in cloud point tests

Equipment:

15 ml transparent covered glass bottle in heated water bath, magnetic stirrer, septum, and thermometer.

Method:

1. 10 wt% aqueous solution of all the surfactants were prepared by distilled water into 15 ml transparent covered glass bottle, in which air should be as less as possible in case to influence the result.

2. The bottle was put into water bath with a magnetic stirrer and was heated from 5 degrees to 100 degrees which was measured by thermometer in the bath.

3. The temperature was recorded when the solution became cloudy.

3.3.3 Foaming Ability

Another relevant feature of surfactants is their foaming ability. A preliminary test has been made using the “cylinder shake test”.[104] The method is used to determine the ability of the solution to foam and stability. The concentration of the foam solution, the temperature and the quality of the water used to prepare the solution will affect the results.

Equipment:

100 ml cylinder with glass top as Figure 32 (the cylinder should have a volume mark of less than 5 ml for the most accurate measurement), foam solution, 10 ml pipette, stopwatch.

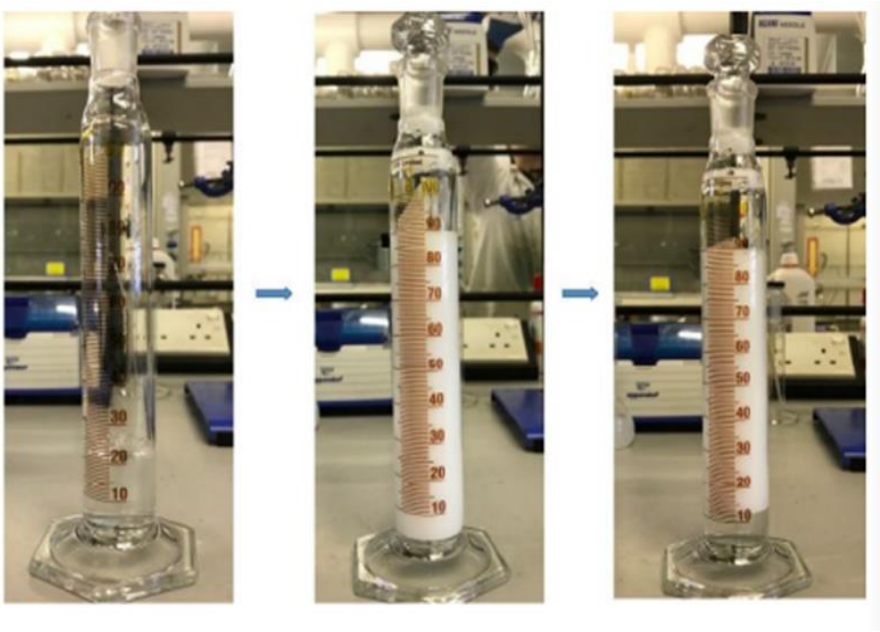


Figure 32 Equipment used in foaming tests

Method:

1. Solution of the product of 1 wt% concentration was prepared by distilled water under room temperature.

2. All the details of the solution were recorded.

3. 20 ml of prepared foam solution was added to the cylinder using a pipette and then the glass stopper was insert onto it.

4. Then the cylinder was shaken vertically and vigorously for ten seconds while holding down the stopper with one finger.

5. After the vibration is complete, the timer was started immediately and the total volume of the foam in the cylinder was recorded in the meantime.

6. If the level is uneven, the average quantity was taken into account.

7. The volume of liquid at the bottom of the cylinder was measured and recorded at

1, 2, 3, 4, 5, 10 and 15 minutes.

8. Foam expansion was calculated using the following formula:

Equation 10

$$Foam\ expansion = \frac{Foam\ volume}{The\ amount\ of\ solution}$$

4 Results and discussion

4.1 Alkyl glyceryl ethers

4.1.1 The results of synthesis of alkyl glyceryl ethers from glycidol with fatty alcohols

As expected, most of these products (alkyl glyceryl ethers) possess surfactant properties as observed when they are mixed with deionised water as the foaming became apparent. After all the purification steps described in the experimental section, relatively low yields were achieved: 23.7% yield of 1-o-octylglycerol, 22.68% yield of 1-o-decylglycerol, 23.67% yield of 1-o-dodecylglycerol, 27.76% yield of 1-o-tetracylglycerol, 21.46% yield of 1-o-hexadecylglycerol, 23.85% yield of 1-o-octadecylglycerol as pure products were analyzed by ^{1}H-NMR. The yields of the reactions are not very high comparing with the highest yield (37%) ever reported for the etherification of glycerol with 1-dodecanol[13] and the 87% yield synthesis of 1-Isobutoxy-3-chloropropanol from epichlorohydrin (ECH) via heterogeneous catalysis.[105] Here, the reactions were run at 140 °C and require a very low addition rate for the EP because of the high activity of EP which would lead to ring-opening self-polymerisation. Therefore, it maybe not easily to control the conversion in the real industry manufacture. On the positive side, ^{1}H –NMR spectra of all these product show that these products were isolated in high purity (Figure 33).

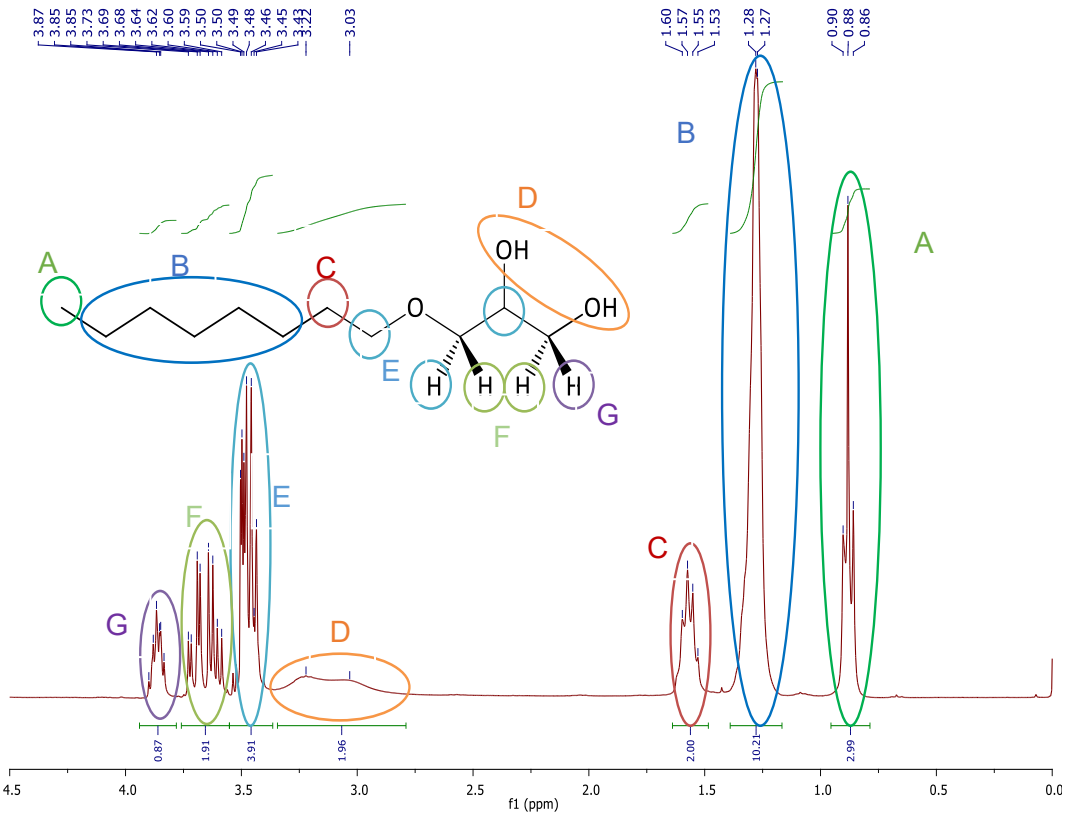


Figure 33 [1]H-NMR spectrum ($CDCl_3$) of 1-o-octylglycerol

[1]H-NMR results of 1-o-octylglycerol (300 MHz, $CDCl_3$) δ: 0.88 (t, ^3J=6 Hz, 3H), 1.28 (s, 10H), 1.56 (m, 2H), 3.03 (br s, 1H), 3.22 (br s, 1H), 3.43~3.50 (m, 4H), 3.50-3.64 (m, 2H), 3.68-3.87 (m, 1H).

1-o-decylglycerol: [1]H-NMR (300 MHz, CDCl3) δ: 0.88 (t, ^3J=6 Hz, 3H), 1.26 (s, 13H), 1.56 (m, 2H), 2.90~4.41 (m, 10H).

1-o-dodecylglycerol:[1]H-NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, ^3J=6 Hz, 3H), 1.26 (s, 18H), 1.56 (m, 2H), 1.70~3.33 (m, 2H), 3.358~3.92 (m, 7H).

To make a more precise judgment of the product purity, [13]C-NMR, Mass Spectrometry (MS) and High Performance Liquid Chromatography (HPLC) were also used for analysis.

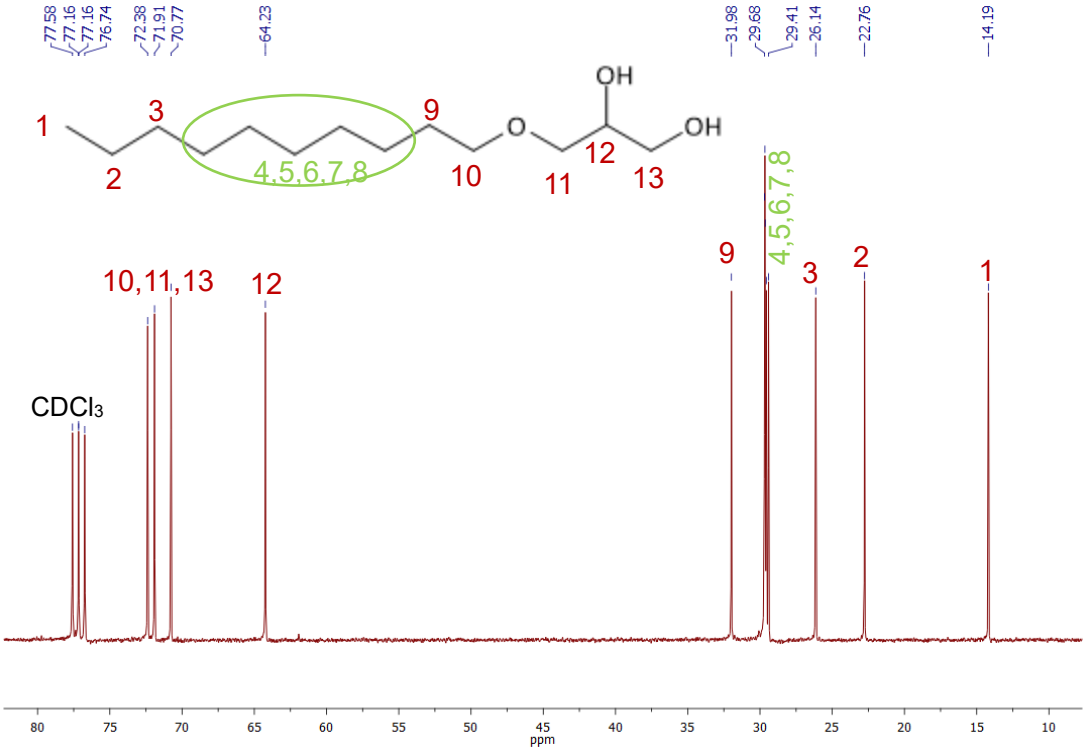


Figure 34 ^{13}C-NMR spectrum ($CDCl_3$) of 1-o-decylglycerol

As Figure 34, ^{13}C-NMR result of 1-o-decylglycerol (300 MHz, $CDCl_3$) shows that the purity of product after column is very high as the number and chemical shift of peaks match the product structure.

As seen in Figure 35, the result of mass spectrometry (MS), the highest peak is 255.1939. Because the molecule mass of 1-o-decylglycerol is 232.360 g and sodium is 23 g, the result matches the expected product.

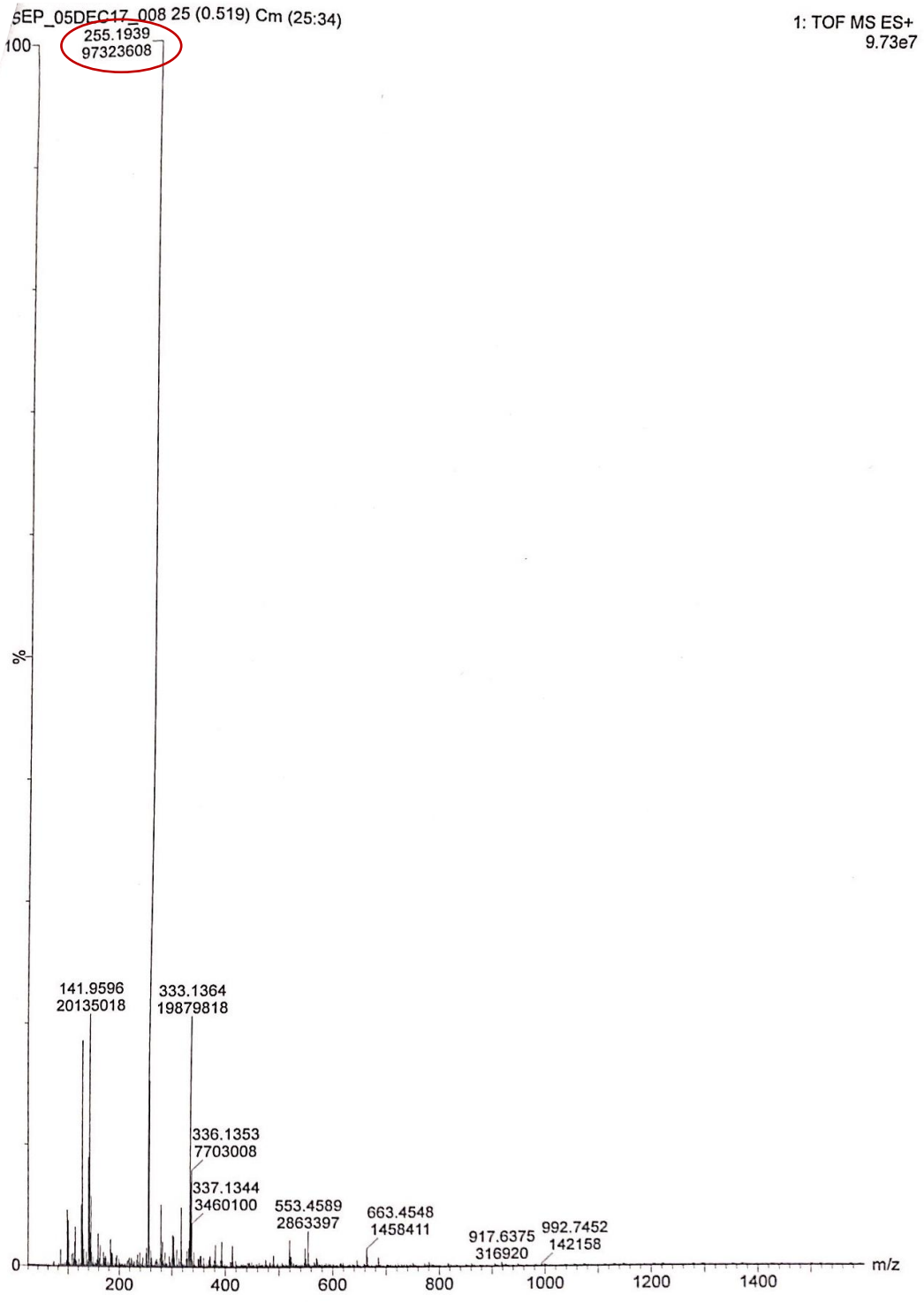


Figure 35 Mass spectrometry result of 1-o-decylglycerol (Na^+)

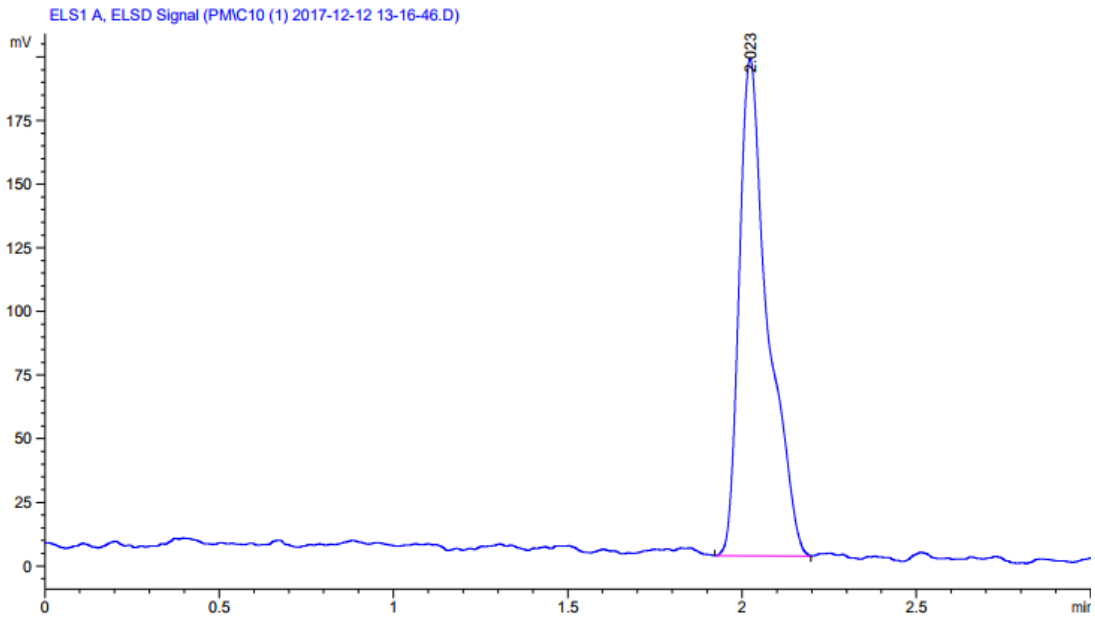


Figure 36 HPLC result of 1-o-decylglycerol (1 mg/m in Methanol)

According to Figure 36, HPLC shows only one peak which means the purity of 1-o-decylglycerol is very high. Combining the results from NMR, MS and HPLC, a conclusion can be gotten that the purity of products after column is very high (>90%).

Pure 1-o-octylglycerol, 1-o-decylglycerol, 1-o-dodecylglycerol, 1-o-tetracylglycerol, 1-o-hexadecylglycerol and 1-o-octadecylglycerol are white solid (their appearance matched the calculation results and known information in Table 7). They all can foam with water even in the presence of some alcohol.

Table 7 The yield and some properties of synthesized alkyl glyceryl ethers. (Pure or crude means the product after or before column. Boiling points and densities are found from ChemSpider. Melting points were calculated by ChemDraw®)

Surfactant	Purity	Yield of EP (%)	Property	Boiling Point	Melting Point	Density
1-o-octylglycerol	Crude	41	Yellow liquid	-		
1-o-octylglycerol	Pure	24	White solid	331.8±22.0 °C at 760 mmHg	68.95 ±1°C	1.0±0.1 g/cm3
1-o-decylglycerol	Crude	39	Yellowish liquid	-		
1-o-decylglycerol	Pure	23	White solid	361.7±22.0 °C at 760 mmHg	91.49 ±1°C	0.9±0.1 g/cm3
1-o-dodecylglycerol	Crude	56	White solid	-		
1-o-dodecylglycerol	Pure	24	White solid	390.5±22.0 °C at 760 mmHg	114.03 ±1°C	0.9±0.1 g/cm3
1-o-tetradecylglycerol	Crude	64	White solid	-		
1-o-tetradecylglycerol	Pure	28	White solid	386.0±17.0 °C at 760 mmHg	136.57 ±1°C	0.9±0.1 g/cm3
1-o-hexadecylglycerol	Crude	50	White solid	-		
1-o-hexadecylglycerol	Pure	21	White solid	464.8±25.0 °C at 760 mmHg	159.11 ±1°C	0.9±0.1 g/cm^3
1-o-octadecylglycerol	Crude	56	White solid	-		
1-o-octadecylglycerol	Pure	24	White solid	471.1±25.0 °C at 760 mmHg	181.65 ±1°C	0.9±0.1 g/cm^3

The conventional catalysts for the synthesis of monoether are homogeneous base catalysts (NaOH, KOH). The reaction rate of EP and monoether exceeds the reaction rate with alcohol. Industry controls the selectivity by increasing the amount of alcohol, but adding a lot of alcohol will inevitably increase operating costs. Changing the process conditions can also improve the selectivity and yield,[106,107] but in general the yield is not high.

4.1.2 Properties of alkyl glyceryl ethers

4.1.2.1 CMC of alkyl glyceryl ethers

The CMC values were calculated for the synthesized compounds, both crude and purified (column chromatography). 1-o-Dodecylglycerol, 1-o-tetradecylglycerol, 1-o-hexadecylglycerol and 1-o-octadecylglycerol were insoluble in water and could not be measured. Each sample was measured ten times and average surface tension was chosen as shown in Table 8.

Table 8 Example of measurement results of 0.1g/L of pure 1-o-octylglycerol

Run-No	CA(M)	ST	Err	Vol
1	0	56.82	0.95	17.02
2	0	56.86	0.79	16.96
3	0	56.76	0.64	16.98
4	0	56.62	0.77	17.03
5	0	56.58	0.71	16.81
6	0	56.38	0.8	16.8
7	0	56.01	0.71	16.65
8	0	55.95	0.79	16.71
9	0	56.05	0.73	16.75
10	0	55.93	0.93	16.61
Average		56.396		

Then all the average surface tensions were drawn in a graph. It is obviously that during the CMC test, surface tension decreases rapidly from the beginning and becomes flat with the concentration increasing, then it would be constant after a certain concentration (Figure 37). Comparing dilute NIS solution and pure water (CMC=72 $mN \cdot m^{-1}$), the surface tension value decreases sharply in dilute solution, which means that the surfactant molecules are adsorbed at air-water interface. When the concentration of the non-ionic surfactant is increased, the surface tension will gradually decrease. When the concentration of the surfactant reaches a critical value, the surface tension will stop decreasing and maintain a constant value. This indicates that the air interface has been saturated with non-ionic surfactant molecules.

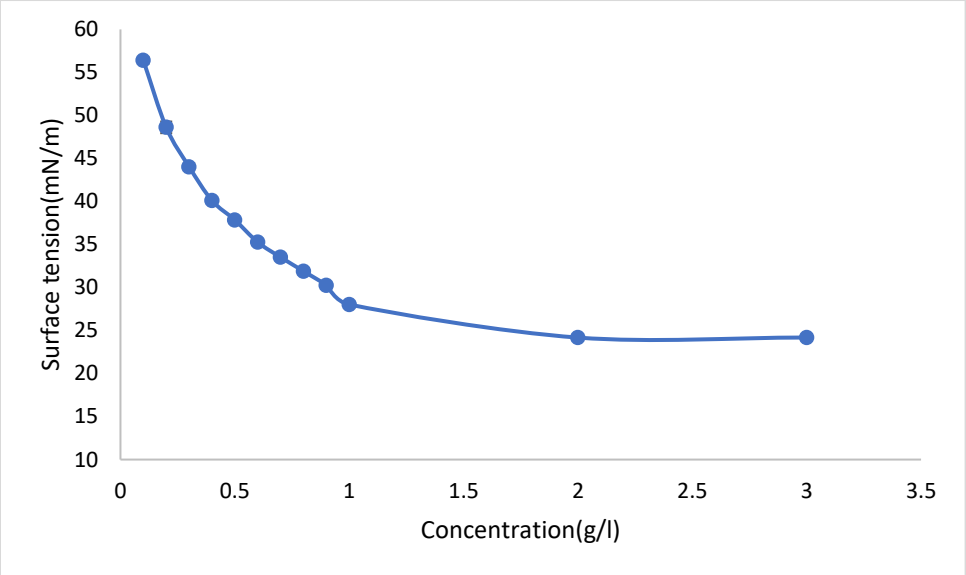


Figure 37 Surface tension at different concentration of 1-o-octylglycerol

The common procedure to determine the CMC from experimental data is to look in a graph where the measured surface tension versus the base 10 logarithm of the surfactant concentration is plotted. The CMC is found at the intersection point of two straight trend lines which represent the two different slopes that can be observed before and after the CMC is reached. The cross point is considered to be the CMC point (Figure 38).

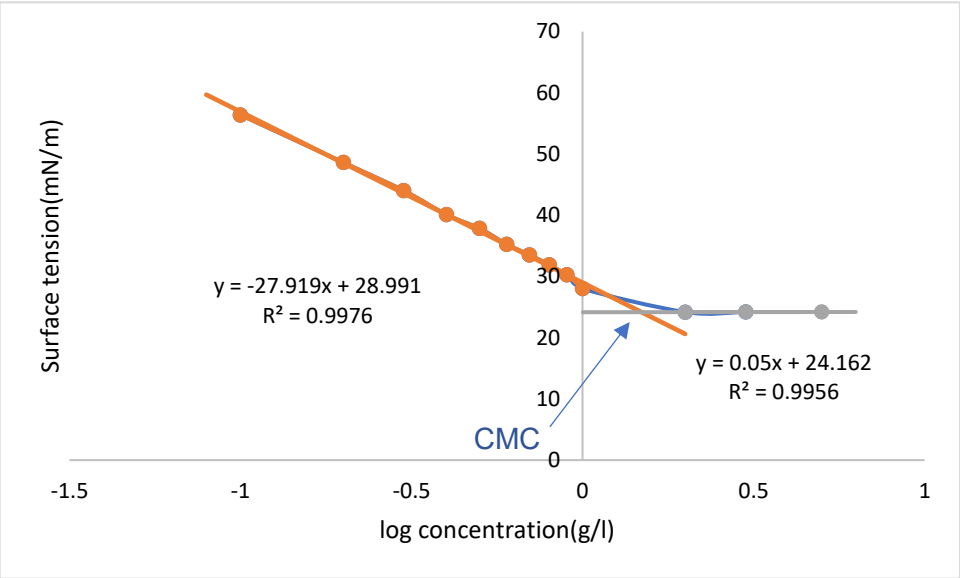


Figure 38 Plot of surface tension with respect to surfactant concentration for 1-o-octylglycerol

The arrow shows the turning point during the decreasing of surfactant concentration versus surface tension, and that is critical micelle concentration (CMC) as mentioned. NIS molecules form micelles in aqueous solution with NIS surfactant concentration increasing. At room temperature, most of the surface tensions at CMC were about 26.0 $mN \cdot m^{-1}$. A lower CMC means a better surface activity. Comparing with the CMC values of other surfactants, the CMC value of 1-o-octylglycerol was lower that of other bio-based surfactants, and 1-*o*-decylglycerol surfactants were even lower, which means these surfactants have better surface activity. From Figure 37, surface tension can decline to 26 $mN \cdot m^{-1}$ because surfactant can be adsorbed at the air-water interface.

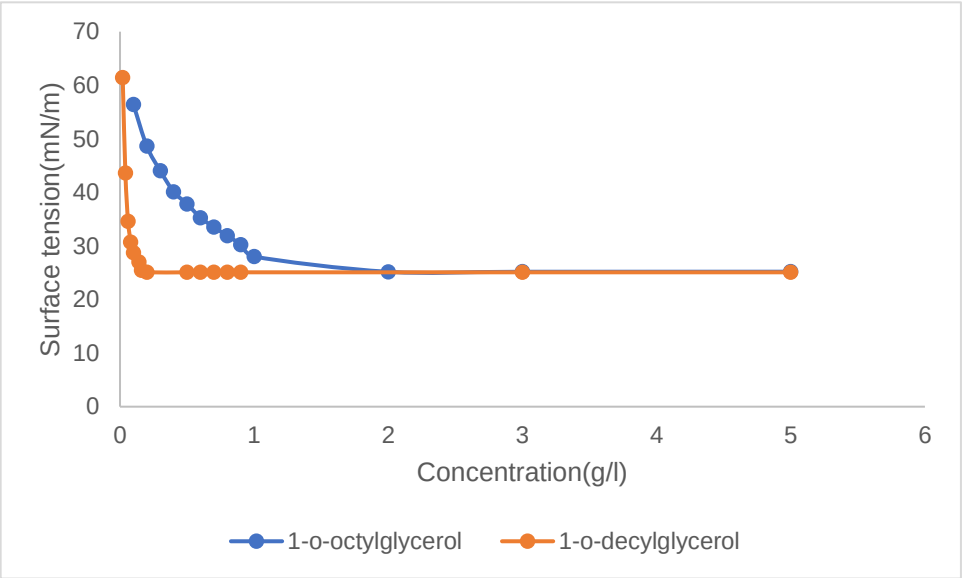


Figure 39 Comparison of surface tension of aqueous solutions of 1-o-octylglycerol and 1-o-dectylglycerol

From Figure 39, the surface tension of 1-o-dectylglycerol decreases faster than 1-o-octylglycerol with concentration rising up which means that it has a better performance as surfactant in aqueous solution.

Table 9 Summary of the main data of synthesized glyceryl ether non-ionic surfactants.

Surfactant[a]	**Mw (g/mol)**	**CMC (g/L)**	**CMC (mmol/L)**	**Temp (°C)**	**ST at CMC (mN/m)**	**Foaming after 5' (cm)**	**HLB value[b]**
C_8-1G	204.3	1.488	7.52	23.9	24.2	2.0	6.9
C_8-1G (crude)	204.3	1.536	-	25.3	25.6	2.5	6.9
C_{10}-1G	228.3	0.101	0.44	23.6	26.2	2.4	5.9
C_{10}-1G (crude)	228.3	0.244	-	24.2	26.2	3.0	5.9
C_{12}-1G	252.3	Water insoluble					5.0
C_{14}-1G	276.4	Water insoluble					4.0
C_{16}-1G	300.4	Water insoluble					3.1
C_{18}-1G	324.4	Water insoluble					2.1

As shown in Table 9, from 1-o-octylglycerol to 1-o-decylglycerol, CMC drops 10 times as the hydrophobic group is longer. In other researches, 1-o-decylglycerol and 1-o-tetradecylglycerol show a lower CMC value, about 1/10 of CMC of 1-o-decylglycerol, but it can't be measured for our experimental conditions.

Lower carbon chain (< C12) glyceryl ethers synthesized from glycidol and the corresponding fatty alcohol showed good foaming and CMC values close to commercial NIS, especially 1-o-decylglycerol (shown in 4.3). Their good properties make them good candidates for prospect industrial production, where they could find potential applications as wetting agents, water-in-oil emulsion stabilizers and co-emulsifiers.

As for higher carbon chain glyceryl ethers (≥ C12), their CMC could not be measured due to their low solubility in water. They showed surfactant properties during the CMC tests as the surface tension decreases quickly at very diluted concentrations and also it can be experimentally observed their ability to foam in water. Due to their lipophilicity, they can be used as defoaming agents, dispersants for solids in oil and co-emulsifiers for example.

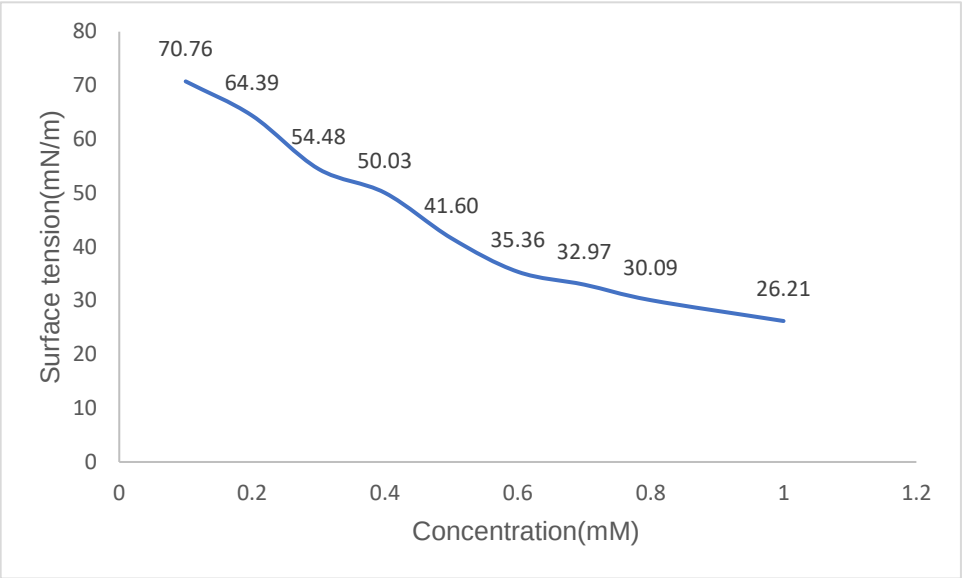


Figure 40 Surface tension at different concentration of 1-o-dodecylglycerol

The solubility of these products will reduce with lipophilic chain getting longer and if the solution is not clear then it cannot be regarded as homogeneous solution which means the result of CMC is not accurate. For example, during the CMC test of dodecylglycerol (Figure 40), the solution of 0.8 mM is not clear and the trend of surface tension at this point is still decreasing so the CMC of this product cannot be measured because its maximum solubility is lower than its potential CMC.

From the results obtained for 1-o-octyl and decylglycerol it can be concluded that the impurities in crude products affected to the overall surfactant behavior, increasing slightly the CMC value and increasing the surface tension of the solution at the CMC point. In general, the main impurities formed during the glyceryl ether synthesis from the fatty alcohols include di- and tri glyceryl ethers, but these are quite difficult to separate from the main product without using expensive chromatographic methods. In any case, all the results fall within the normal range of CMC values of commercial non-ionic surfactants. A classification of non-ionic surfactants according to their solubility in water and their possible areas of application is shown in Table 10.

Table 10 HLB classification for non-ionic surfactants

HLB Range	Behavior in water	Potential application	Surfactant	Commercially available examples
0-3	Insoluble	defoaming agent, dispersant for solids in oil, co-emulsifier, refatting agent	1-*o*-octadecylglycerol	Glycerol trioleate Glycerol dioleate, Glycerol monooleate
3-6	Insoluble, dispersible	water-in-oil emulsions, co-emulsifier	1-*o*-decylglycerol, 1-*o*-dodecylglycerol, 1-o-tetradecylglycerol, 1-*o*-hexadecylglycerol	Glycerol monostearate Propylene glycol monolaurate, Diethylene glycol monolaurate
6-9	Dispersible, giving milky solution	wetting agent, water-in-oil emulsions	1-*o*-octylglycerol	Sorbitan monopalmitate Sorbitan monomyristate Sorbitan monolaurate
8-10	Soluble, giving milky turbid to translucent solutions	wetting agent	Surfactant 3G	Isotridecanol ethoxylate with 3 to 5 ethylene oxide molecules (EO)
10-13	Soluble giving translucent to clear solutions	oil-in-water emulsions, detergents and cleansing agents		Isononylphenol ethoxylate with 5 to 7 EO
13-15	Soluble, giving clear solution	oil-in-water emulsions, detergents and cleansing agents		Octadecanol ethoxylate with 10 to 16 EO
>15	Soluble, giving clear solutions	solubiliser, cleansing agent	Surfactants 6G, 10G, 12G	Dodecanol/tetradecanol ethoxylate with 13-38 EO

For all surfactant samples of aqueous solution, they are all single solute aqueous solution, then Equation 5 (Gibbs adsorption equation) can be transformed to be:

Equation 11

$$\Gamma_{max} = -\frac{CMC}{RT}\left(\frac{d\gamma}{dc}\right)$$

All the slopes were already calculated in the process of calculating the CMC and the crude products cannot be calculated due to that they are mix and completed compound.

According to Table 11, all the value of Γ_{max} and A_{min} were calculated for the adsorption phenomenon occurs on the air-water interface at room temperature.

Table 11 Surface properties of alkyl glyceryl ethers in aqueous solution

Surf.	Temp (°C)	CMC (mmol/l)	γ_0 (mN·m^{-1})	γ_{cmc} (mN·m^{-1})	Π_{cmc} (mN·m^{-1})	Γmax (μmol/m^2)	Amin (m^2/μmol)
C_8-1G	23.9	7.52	72.19	24.17	48.02	18.69	0.01
C_8-1G (crude)	25.3	-	71.97	25.63	46.34	-	-
C_{10}-1G	23.6	0.44	72.24	26.15	46.09	16.17	0.01
C_{10}-1G (crude)	24.2	-	72.15	26.19	45.96	-	-

For the surfactant molecules in the tests, the value of Π_{cmc} can be calculated according to the Equation 3, and from the results it is obviously that they have good ability of decreasing surface tension of the aqueous solution. For some other types of bio-based surfactants, such as N-phenyl fatty amidopropyl-N, zwitterionic surfactants, N-dimethylcarboxylbetaine (PFAPMB), and N-fatty acyl amino acid surfactant (SFAAA), their γ_{cmc} of surfactant aqueous solutions are 28.4 mN·m^{-1}, and 28.0 mN·m^{-1}.[108]

Comparing all the results, the reduced surface tension Π_{cmc}s of all samples are around

46 $mN \cdot m^{-1}$, and the maximum surface excess concentration, Γ_{max}s are high, leading to about 10 μmol/m², which means they are very closely spaced in the surface, and the minimum area A_{min}s are around 10^{-2} m^2/μmol. It is obviously that in NIS molecules, the value of A_{min} is lower than other types of surfactants, and the lower A_{min} can make Γ_{max} value be higher.

Table 12 Properties of two anion surfactants[108]

Surfactant	CMC (mmol/L)	γ_{cmc} ($mN \cdot m^{-1}$)	Π_{cmc} ($mN \cdot m^{-1}$)	Γ_{max} (μmol/m^2)	A_{min} (m^2/μmol)
NDPSS	1.9	28.0	44.0	3.38	49.10
SDS	8.2	32.5	39.5	3.16	53.00

(NDPSS: N-diethoxypropylsulfonate sodium, SDS: sodium dodecyl sulfate)

The CMC of ionic surfactants is much higher than the CMC of non-ionic surfactants. Table 12 gives some properties of two anion surfactants. In general, when the hydrocarbon chain is the same, the former is about 100 times larger than the latter.[109] This is because the hydrophilic groups of the ionic surfactants have a stronger hydration effect with water, and the hydrophilic groups of the non-ionic surfactants have a lower hydrophilicity.

For the cases of 1-o-hexadecylglycerol and 1-o-octadecylglycerol, their CMC values could not be calculated as they are practically insoluble in water, making it impossible to measure them. This fact does not imply that they are not good surfactants, as it is experimentally observed how they form significant foam in contact with different solvents (water, chloroform) and may find application as co-emulsifiers or water-in-oil emulsions (Table 10).

4.1.2.2 Foaming abilities of alkyl glyceryl ethers

After shaking vigorously for ten seconds, the foam formation rose a lot. Liquid volume

rising of each minute would be recorded to identify the foam stability. Regarding the foam stability, the foam height is reduced considerably after 5 minutes (around 30% of the initial foam), which is even a good result for a non-ionic surfactant, as they are naturally less foamy than anionic surfactants such as sodium dodecyl sulfate (SDS).

The type of surfactant is the main factor determining the foaming force, and environmental conditions are also important. For example, the temperature, the hardness of water, the pH value of the solution and additives, have a great impact on the foaming force. The effect of temperature on the foaming power of non-ionic surfactants is different from that of anionic surfactants. For example, when the temperature is lower than the cloud point, the polyethylene ether non-ionic surfactant can have a large volume of foam, but after the temperature is higher than cloud point, the foaming ability starts to reduce. However, anionic surfactants are less sensitive to temperature.

For the alky glyceryl ethers, the pure products after column all performed worse than the products before column, so it can be concluded that the impurities in crude products affected to the overall surfactant behavior, increasing foaming ability. In general, the main impurities formed during the glyceryl ether synthesis from the fatty alcohols include di- and tri glyceryl ethers.

The pure alky glyceryl ethers containing long carbon chain ($\geqslant$12) do not foam well, especially the 1-o-dodecylglycerol which can hardly raise foam. And for 1-o-tetracylglycerol, 1-o-hexadecylglycerol and 1-o-octadecylglycerol, 1 wt% solutions could not be prepared for the standard foam tests due to their low solubility.

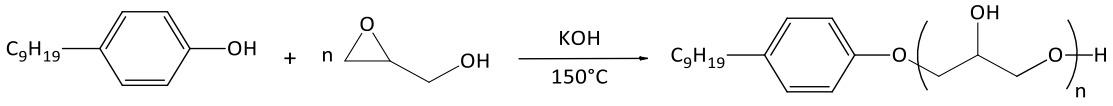
Table 13 The foaming test results of alky glyceryl ethers

	Pure C_8		**Crude C_8**		**Pure C_{10}**		**Crude C_{10}**		**Pure C_{12}**		**Crude C_{12}**	
Mins.	**Volume of liquid (ml)**	**Foam expansion**	**Volume of liquid (ml)**	**Foam expansion**	**Volume of liquid (ml)**	**Foam expansion**	**Volume of liquid (ml)**	**Foam expansion**	**Volume of liquid (ml)**	**Foam expansion**	**Volume of liquid (ml)**	**Foam expansion**
1	16	2.500	12.4	5.685	13	3.462	15.2	4.638	18	1.611	18	3.917
2	19	2.105	15.7	4.490	14.7	3.061	16.9	4.172	18	1.611	18.1	3.895
3	19.5	2.051	17	4.147	16.6	2.711	17.6	4.006	18	1.611	18.2	3.874
4	19.7	2.030	17.8	3.961	17.8	2.528	18.05	3.906	18	1.611	18.3	3.852
5	19.8	2.020	18.1	3.895	18.6	2.419	18.2	3.874	18	1.611	18.3	3.852
10	19.8	2.020	18.9	3.730	19.8	2.273	18.85	3.740	18.1	1.602	18.8	3.750
15	19.8	2.020	19	3.711	19.9	2.261	18.9	3.730	18.2	1.593	18.8	3.750
	Foam (ml)		**Foam (ml)**		**Foam (ml)**		**Foam (ml)**		**Foam (ml)**		**Foam (ml)**	
	40		70.5		45		70.5		29		70.5	

4.2 Nonylphenol poly glyceryl ethers

4.2.1 The results of synthesis of nonylphenol poly glyceryl ethers

Replacing EO by glycidol would lead to products with more hydroxyl groups in the polar head and therefore may have different surfactant properties such as water solubility, CMC or minimum surface tension. Therefore, four different compounds with 3, 6, 10 and 12 glyceryl units respectively were synthesized and characterized. The aim of these compounds is to be an alternative to nonylphenol ethoxylate derivatives, which are highly common family of commercial NIS, and, amongst other companies, produced by Dow under the commercial name “Tergitol-NP-X™”.[110] Industrially, these surfactants are applied as detergents, solubilizers and cleansing agents. Non-ionic surfactants C_9-Φ-G3, C_9-Φ-G6, C_9-Φ-G10 and C_9-Φ-G12, were synthesized by combining nonylphenol and glycidol in 3- and 12-fold excesses, respectively (Figure 41).



Nonylphenol EP

n = 3 C_9-Φ-G3

n = 6 C_9-Φ-G6

n = 10 C_9-Φ-G10

n = 12 C_9-Φ-G12

Figure 41 Base-catalysed synthesis of C_9-Φ-G3, G6, G10, G12 from EP and nonyl-phenol

The reactants were added in ratio according to the expected product in these synthesis. The excess of KOH was reacted with CO_2 to form K_2CO_3 and H_2O which were removed from the product in the extraction step. All of them are obtained as very viscous and sticky brown liquids, which are soluble in water and other polar solvents such as DMSO or methanol. Their purity has been analysed by ^{1}H-NMR.

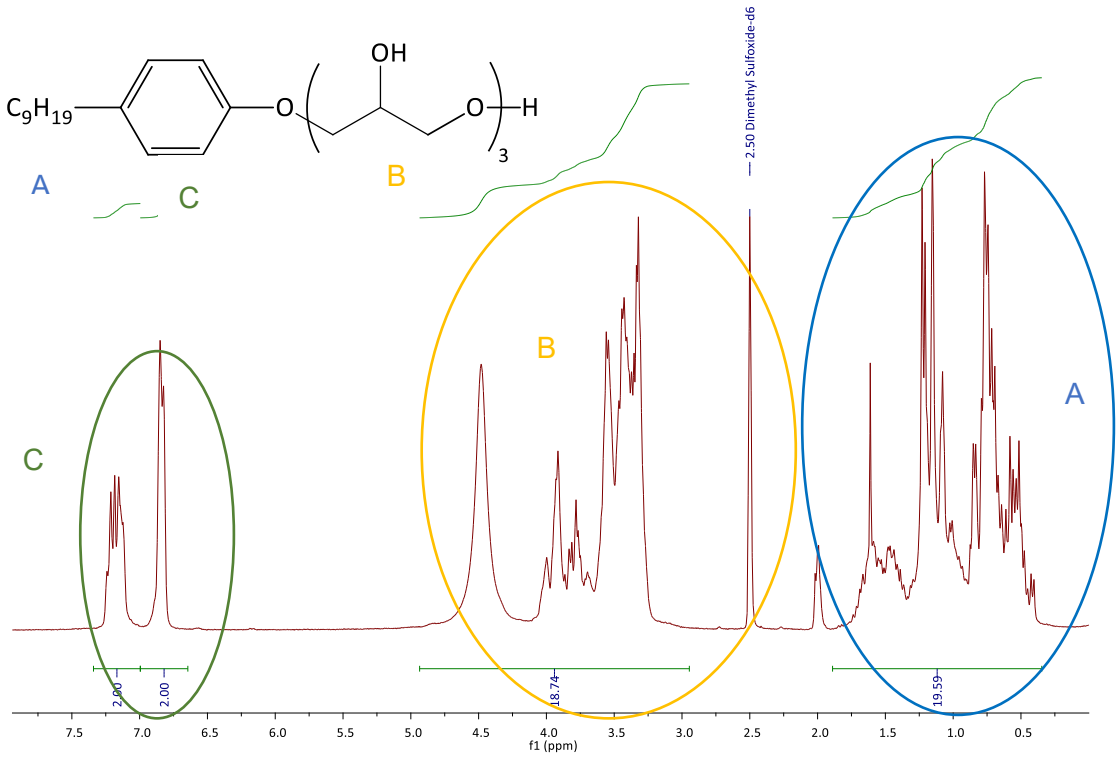


Figure 42 [1]H-NMR spectrum (dmso-d6) of surfactant C_9-Φ-G3

As shown in Figure 42, [1]H-NMR results of C_9-Φ-G3: [1]H NMR (300 MHz, CDCl3) δ: 0.4~1.65 (m, 19H), 2.5 (s, DMSO), 3.25~4.5 (m, 18H), 6.85,6.89 (d, 2H),7.15~7.25 (m, 2H). The peaks show that the product is not very pure but amount of the expected product can be obtain in this synthesis method.

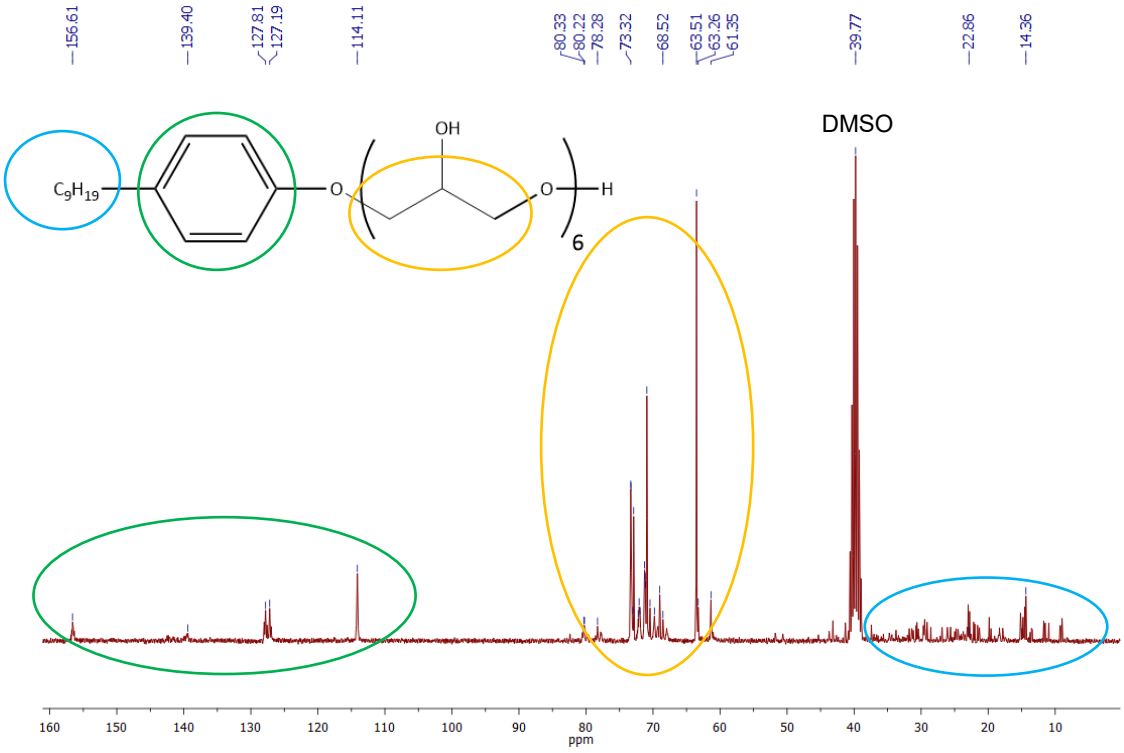


Figure 43 ^{13}C-NMR spectrum (DMSO-d_6) of C_9-Φ-G6

In Figure 43, ^{13}C-NMR spectrum (DMSO-d6) shows that the purity of C_9-Φ-G6 is not very high. As there are many isomers of linear alkyl in starting material, nonylphenol, the peaks in ^{13}C-NMR spectrum are a bit messy. This can explain those small peaks in the figure.

for the result of MS, shown in Figure 44, the peak of 687.3932 is the expected oduct (C_9-Φ-G6) and the peak of C_9-Φ-G3 is the highest one. This result shows that e product is obviously a mixture. G6 molecule has six ether bonds which are easily be broken by electron bombardment during MS analysis, so this can explain why aks (391, 465, 539, 613, 687) have a different of 74, which is exactly the molecule mass value of glycidol. Although the ether bond is easily to be broken, the most important reason is that C_9-Φ-G3 is the main product. This also appeared in MS analysis of G10 and G12. In G10 (Figure 45), C_9-Φ-G5 is the main product, which means excess ratios of glycidol need to be added to get expected product.

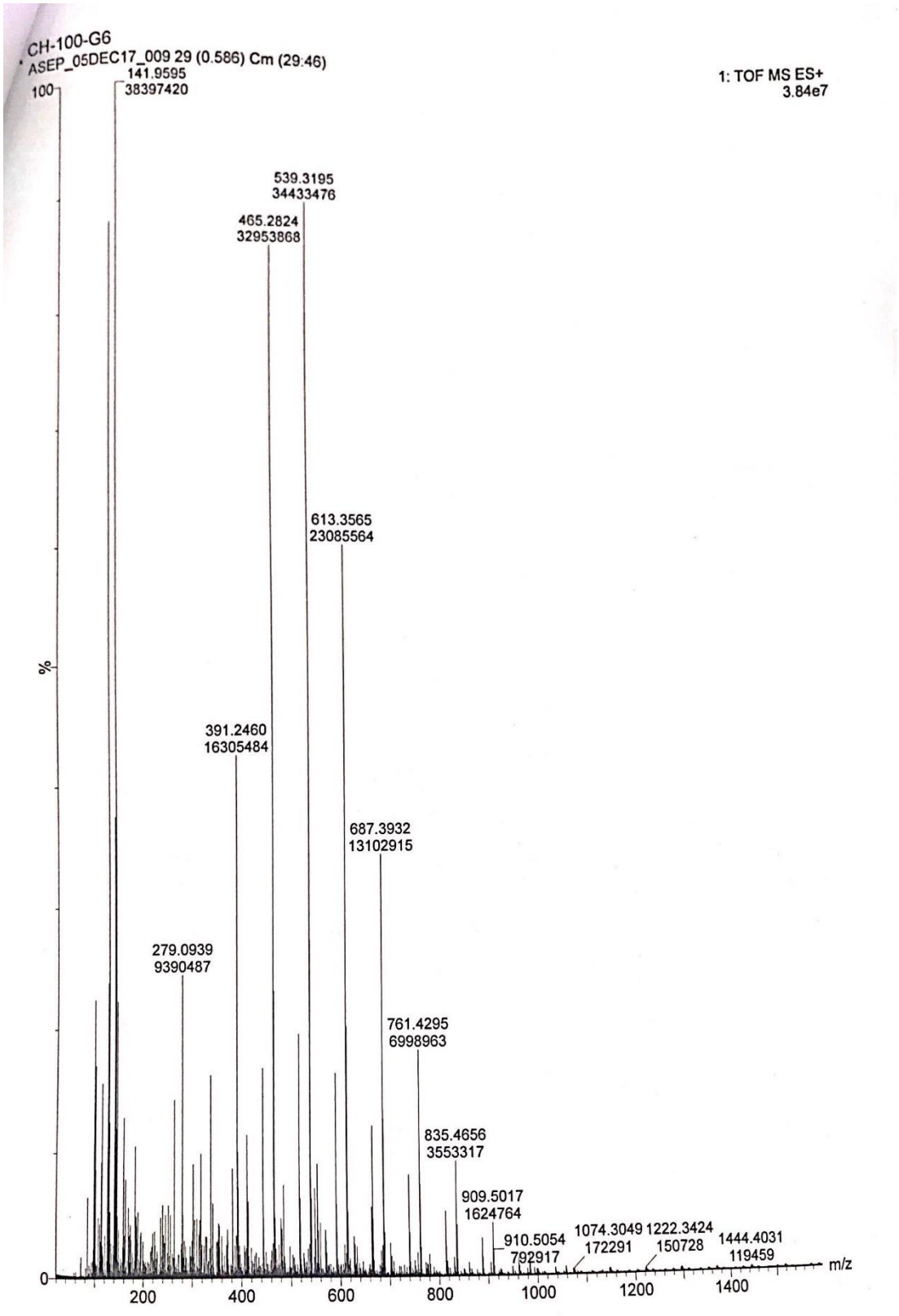


Figure 44 Mass spectrometry result of C_9-Φ-G6 (Na^+)

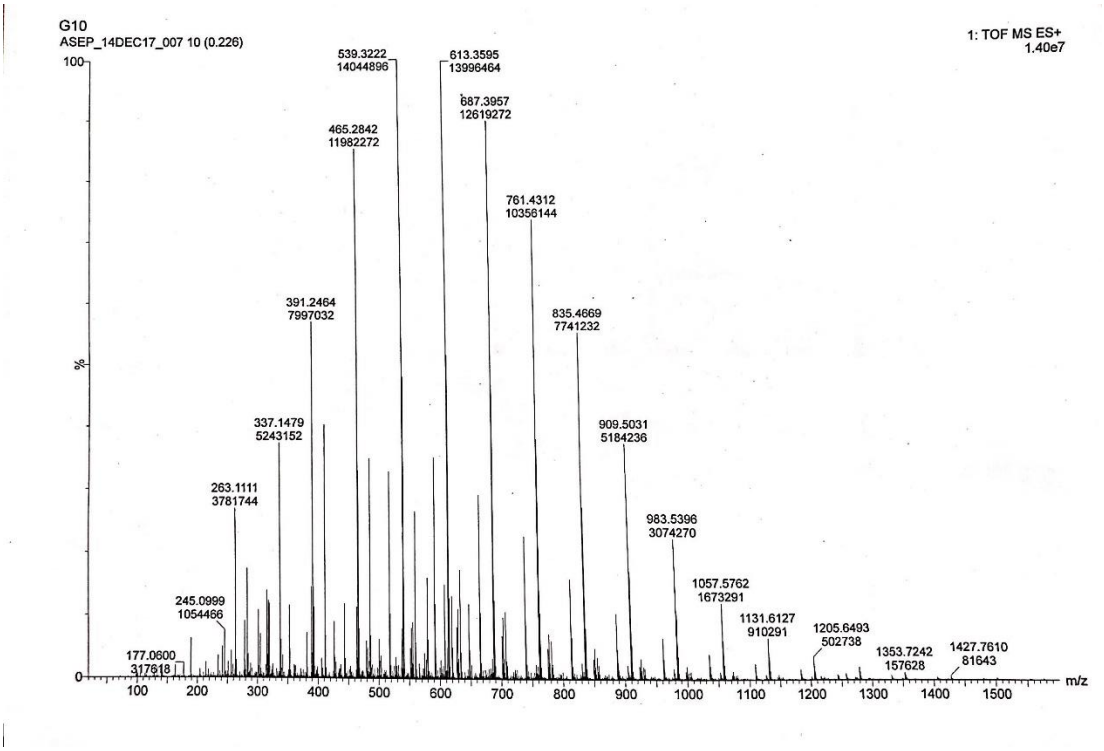


Figure 45 Mass spectrometry result of C_9-Φ-G10 (Na^+)

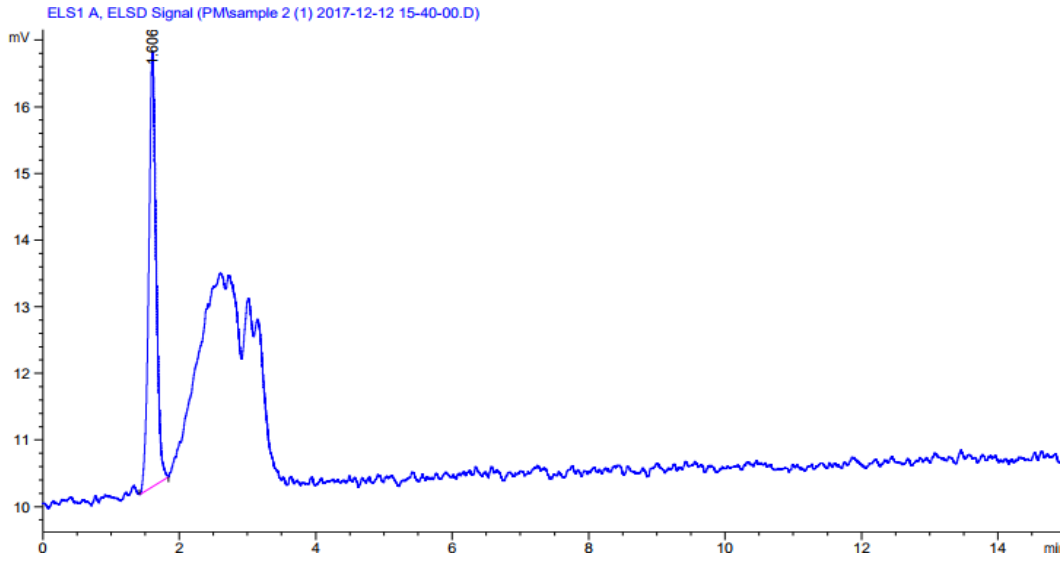


Figure 46 HPLC result of C_9-Φ-G6 (1 mg/m in Methanol)

The HPLC result (Figure 46) also shows there are some other compounds in the product as the product is polymer and the starting material also has some isomers.

All the analysis shows a statistical mixture of products, which means products from

nonylphenol are not very pure and to obtain expected product, excess ratios of glycidol needs to be added. Refined calculation of the relationship between reactant ratio and product structure needs to be researched in the further work.

As the products have more hydrophilic groups than alkyl glyceryl ethers, they do not dissolve in $CDCl_3$ and their ^{1}H-NMR analysis had to be carried out using DMSO-d_6. Some properties are shown in Table 14.

Table 14 The synthesis results of nonylphenol poly glyceryl ethers

Surfactant	Appearance	HLB
C_9-Φ-G3	Brown Liquid	10.0
C_9-Φ-G6	Brown Solid	15.3
C_9-Φ-G10	Brown Solid	22.4
C_9-Φ-G12	Brown Solid	25.9

4.2.2 Properties of nonylphenol poly glyceryl ethers

4.2.2.1 CMC of nonylphenol poly glyceryl ethers

Surface tension measurement was conducted to study the surface properties of nonylphenol poly glyceryl ethers as surfactant in aqueous solution. As he products of nonylphenol poly glyceryl ethers showed good solubility in aqueous solution, the CMC test was easy to proceed. Table 15 shows the surface properties of nonylphenol poly glyceryl ethers in aqueous solution.

Table 15 Surface properties of nonylphenol poly glyceryl ethers in aqueous solution

Surfactant	Temp (°C)	CMC (g/L)	CMC (mmol/L)	γ_0 (mN·m^{-1})	γ_{cmc} (mN·m^{-1})	Π_{cmc} (mN·m^{-1})	Γ_{max} (μmol/m^2)	A_{min} (m^2/μmol)
C_9-Φ-G3	23.9	0.125	0.28	72.19	35.36	36.83	21.38	0.01
C_9-Φ-G6	23.7	0.11	0.17	72.22	31.02	41.2	16.56	0.01
C_9-Φ-G10	24.4	0.251	0.26	72.12	29.88	42.24	10.36	0.02
C_9-Φ-G12	24	0.621	0.56	72.18	33.22	38.96	19.75	0.01

Their CMCs were also determined, leading to higher values than those of commercial ethoxylates but with lower surface tension at the CMC, which is also a good sign for any surfactant. This is expected as replacing the ethoxylate groups in the latter by glyceryl groups increases the size of the surfactant's polar head, which is known to increase the CMC.[111]

The γ_{cmc} and Π_{cmc} values of the C_9-Φ-G6 and C_9-Φ-G10 increased slightly as compared to C_9-Φ-G3 surfactant. It is clear that the minimum surface area of the surfactant molecule A_{min} increases when the number of glyceryl ether units in the nonyl phenol surfactants increases. The low value of A_{min} indicates that the air / water interface is sealed; therefore, the orientation of the surfactant molecules at the interface is almost perpendicular to the interface.[108] At the same time, the areas of the C_9-Φ-G6 and C_9-Φ-G10 surfactant molecules are larger than that of C_9-Φ-G3, indicating that the surfactant molecules are not folded at the air-water interface. Due to the interaction between the chain becomes stronger, the minimum surface area of surfactant C_9-Φ-G12 molecules, decreases.

Table 16. Summary of the data of synthesized nonylphenol-based non-ionic surfactants.[110]

Surfactant	Mw (g/mol)	CMC (g/L)	CMC (mmol/L)	Temp (°C)	ST at CMC (mN/m)	Foaming after 5' (cm)	HLB value
C_9-Φ-3G	442.6	0.125	0.28	23.9	35.36	1.3	10
TERGITOL NP-4	423.5			Water insoluble			8.9
C_9-Φ-6G	664.8	0.110	0.17	23.7	31.0	3.1	15.3
TERGITOL NP-6	511.5			Water insoluble			10.9
C_9-Φ-10G	887.0	0.251	0.28	24.4	29.9	3.4	>20
TERGITOL NP-10	687.6	0.055	0.08	25.0	33.0	11.0	13.2
C_9-Φ-12G	1109.3	0.621	0.56	24.0	33.2	3.7	>20
TERGITOL NP-12	775.7	0.085	0.11	25.0	35.0	11.5	13.8

The hydrophilic – lipophilic balance (HLB) value of a surfactant determines if the whole molecule will be hydrophilic (soluble in water) or lipophilic (insoluble in water). This parameter is very useful to classify non-ionic surfactants as the HLB of a particular one can give an idea of its potential application in industry.

Table 16 shows the comparison of properties between nonylphenol poly glyceryl ethers and similar commercial products, TERGITOL NPX. For the excellent detergency and outstanding wetting of TERGITOL NPX, they have already been used in cleaners & detergents, paper & textile processing, paints & coatings, agrochemicals and metalworking fluids. The products of C_9-Φ-GX here have more -OHs so they have higher CMC values and HLB values. In this condition, according to Table 10, they can also be used in oil-in-water emulsions, detergents and

cleansing agents and solubiliser,

4.2.2.2 Foaming abilities of nonylphenol poly glyceryl ethers

As for the NIS products based on nonyl phenol, their foam volume increases as the hydrophilic group getting bigger, in which the product with C_9-Φ-G3 did not foam well just like 1-o-dodecylglycerol. So, it can be concluded that the low solubility can cause low foaming ability and for these in low foaming ability, they can be used as defoaming agents, dispersants for solids in oil and co-emulsifiers for example.

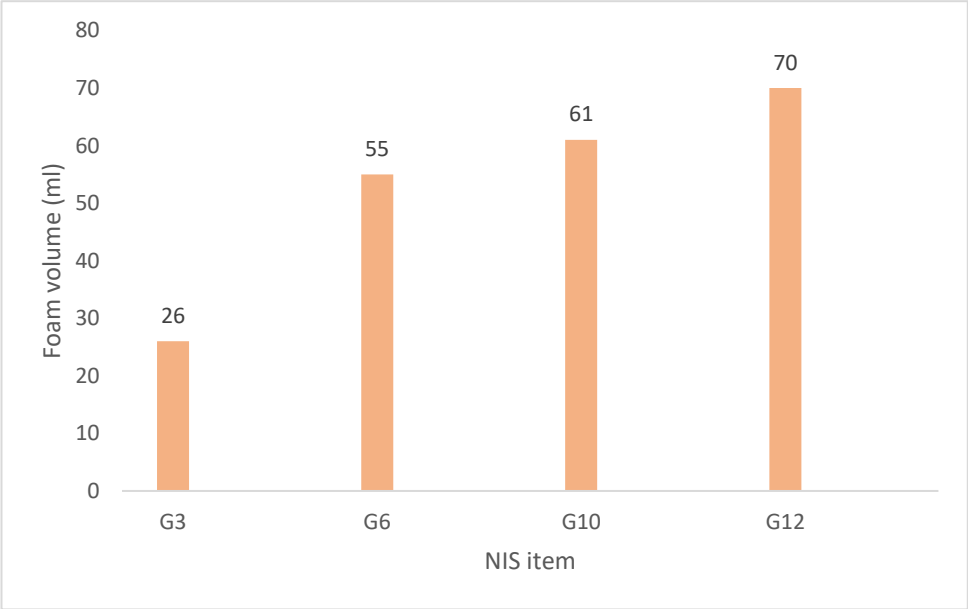


Figure 47 Foaming ability of Surfactant C_9-Φ-G3 to G12

According to Figure 47, C_9-Φ-G3 has a bad foam stability and the foam disappeared much more quickly than for the other surfactants tested.

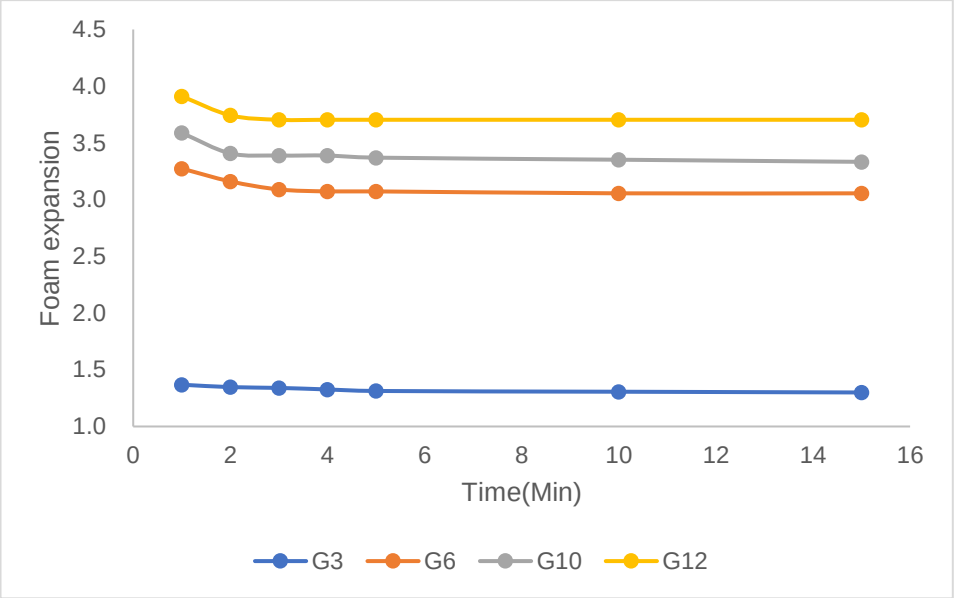


Figure 48 Foam expansion of Surfactant C_9-Φ-G3 to G12

C_9-Φ-G12 has the best foaming ability and foam stability (Figure 48) so it can be used in many industry products required good foaming ability such as detergents.

4.3 Poly(glyceryl)ethers

4.3.1 Catalyst optimization

The catalysts used in the etherification of alkylene oxide and alcohols are mainly divided into three main categories: acid (protonic acid, Lewis acid), base and salt. In terms of mechanism, the base catalyst mainly activates alcohol to alkoxy anion and the activated alcohol and EP are easy to form polyether. However, acidic catalyst mainly activates EP, making contribution to the formation of positive carbon ions and then the activated EP reacts with the alcohol to form an alcohol ether. When using a Lewis acid catalyst, the selectivity of monoether is high, but it is easy to produce by-products. It has been proved that in the etherification reaction of ethylene oxide and alcohol, traditional alkaline catalyst will make the reaction easy to form polyether.

$La(OTf)_3$, as a Lewis acid catalyst, was tested in this reseach. The reactions of

synthesis polyglyceryl ether C_{12}-3G and C_{12}-6G with $La(OTf)_3$ as catalyst have been proved to be very effective and the ^{1}H-NMR analysis of the surfactant C_{12}-3G is as follows as example.

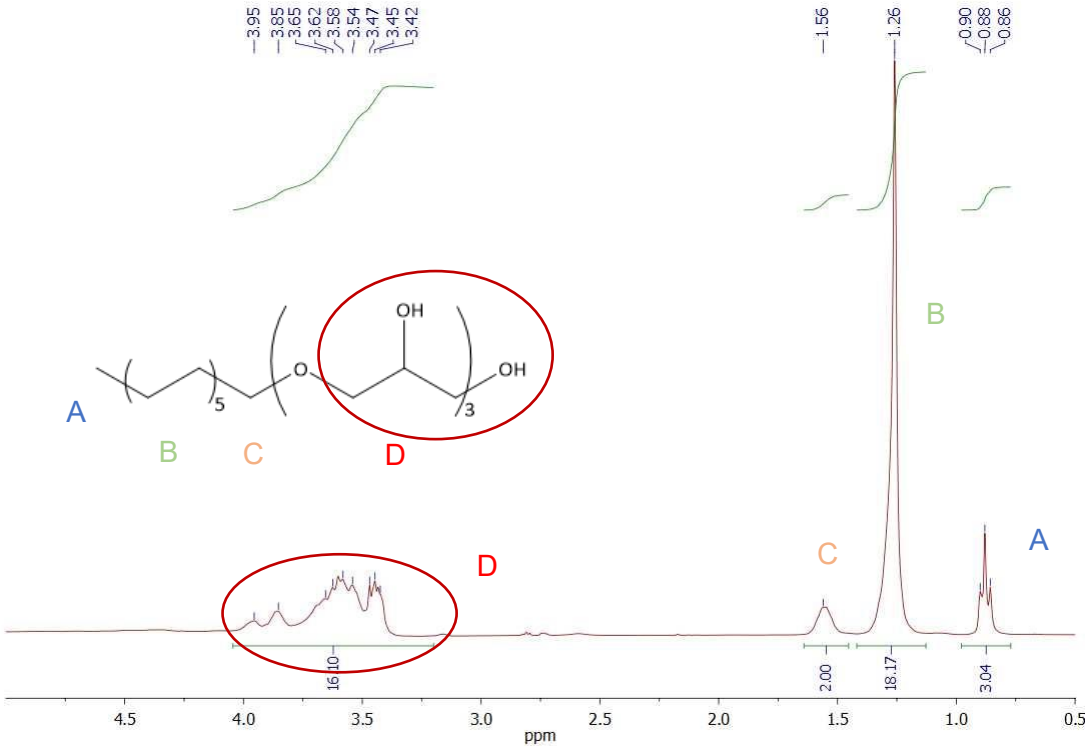


Figure 49 ^{1}H-NMR spectrum in $CDCl_3$ of the surfactant C_{12}-3G using $La(OTf)_3$ as catalyst

Figure 49 shows the result of C_{12}-3G using $La(OTf)_3$ as catalyst in ^{1}H NMR (300 MHz, CDCl3) δ: 0.88 (t, *J* = 6.0 Hz, 3H), 1.26 (s, 18H),1.56 (m, 2H), 3.20 –4.04 (m, 16H). In this reaction, the operation of purification step is simpler than the purification of alkyl glyceryl ethers, only need a silica column chromatography to remove impurities.

Although very high conversions and selectivities to the final product have been achieved using $La(OTf)_3$, has many drawbacks that makes complicated its use in industry, such as its complex and costly production and corrosive action on equipment. Cheaper alternatives are needed to be tested in order to make it economically viable for industrial scale ($La(OTf)_3$ = 6.5 £/gram, Sigma-Aldrich).

The same reaction using Amberlyst 15 as catalyst in the same condition was not successful. Amberlyst 15 is a macro reticular polystyrene based ion exchange resin with strongly acidic sulfonic group, which has excellent performance in catalytic etherization.[112] Although the product was a turbid brown. ^{1}H-NMR analysis shows that no expected products were obtained.

Then Iron(III) chloride ($FeCl_3$) was tried for synthesis of polyglyceryl ether C_{18}-6G and C_8-6G because Iron(III) chloride is a cheaper Lewis acid than $La(OTf)_3$ and it can catalyze reductive etherification of carbonyl compounds with alcohols.[113] Although the product was not clear, ^{1}H-NMR analysis shows that no expected products were obtained.

The reaction of synthesis polyglyceryl ether C_{12}-3G without catalyst has been proved to be not happening as the ^{1}H-NMR analysis only show dodecanol and glycidol existing.

Then the reactions of synthesis polyglyceryl ether C_{12}-3G and C_{12}-6G with potassium hydroxide (KOH) as catalyst also had a good performance.

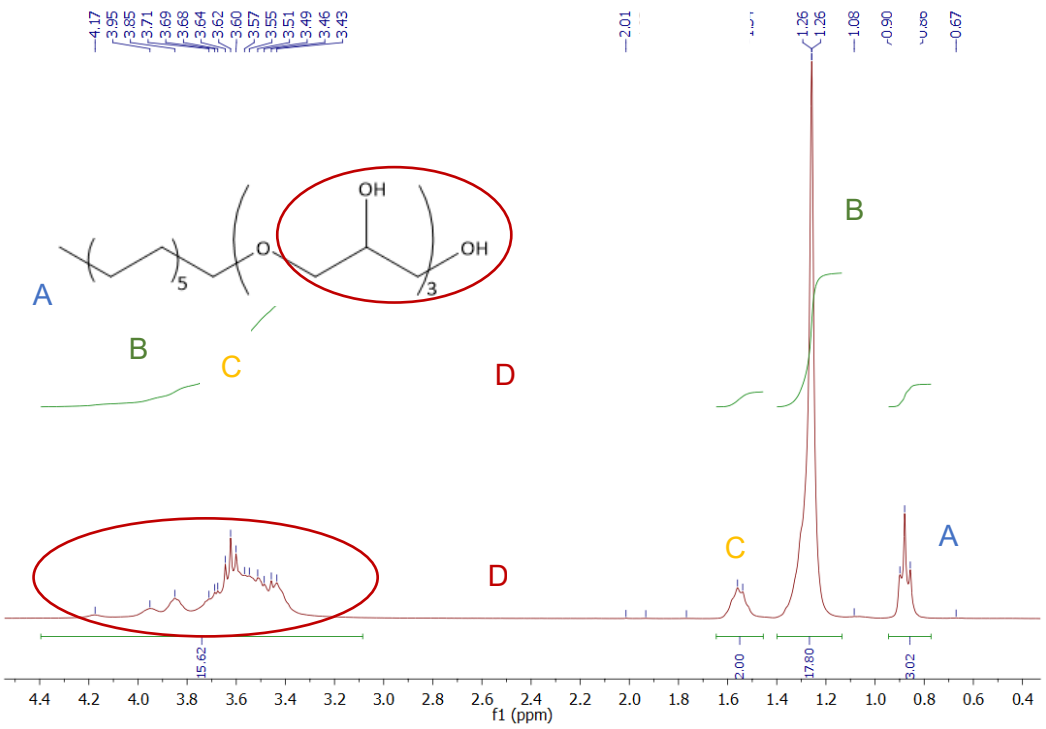


Figure 50 ^{1}H-NMR spectrum in $CDCl_3$ of the surfactant C_{12}-3G using KOH as catalyst

Figure 50 shows the result of C_{12}-3G using KOH as catalyst in ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, *J* = 6.0 Hz, 3H), 1.13–1.40 (m, 17H), 1.55 (m, 2H), 3.09–4.40 (m, 16H). The purification step is the same as the synthesis using $La(OTf)_3$.

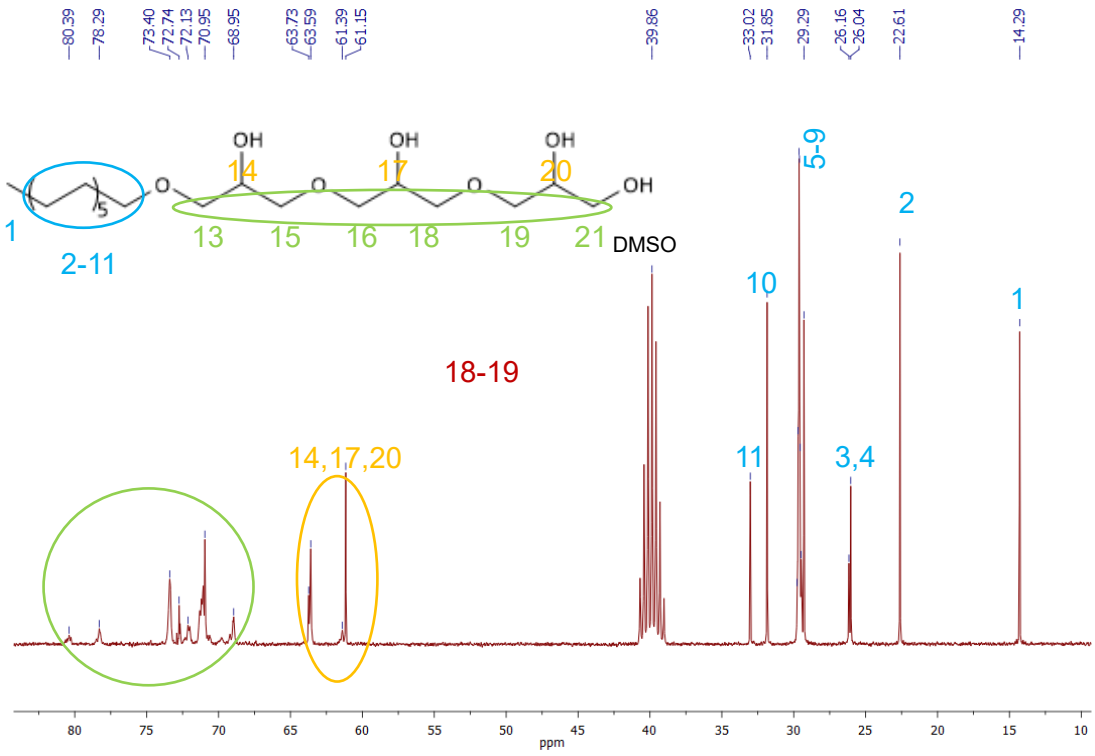


Figure 51 ^{13}C-NMR spectrum (DMSO-d_6) of C_{12}-3G using KOH as catalyst

As Figure 51, ^{13}C-NMR result of C_{12}-3G (300 MHz, DMSO-d_6) shows that the purity of product after column is high as the number of peaks matches the product structure.

In Figure 52, the MS result of C_{12}-3G shows that the product is the expected compound as the highest peak is 431.2982 (molecule mess of C_{12}-3G is 408.57 g). Also because of ether bonds broken and by-product produced, the difference between adjacent peaks to the expected product peak is 74.

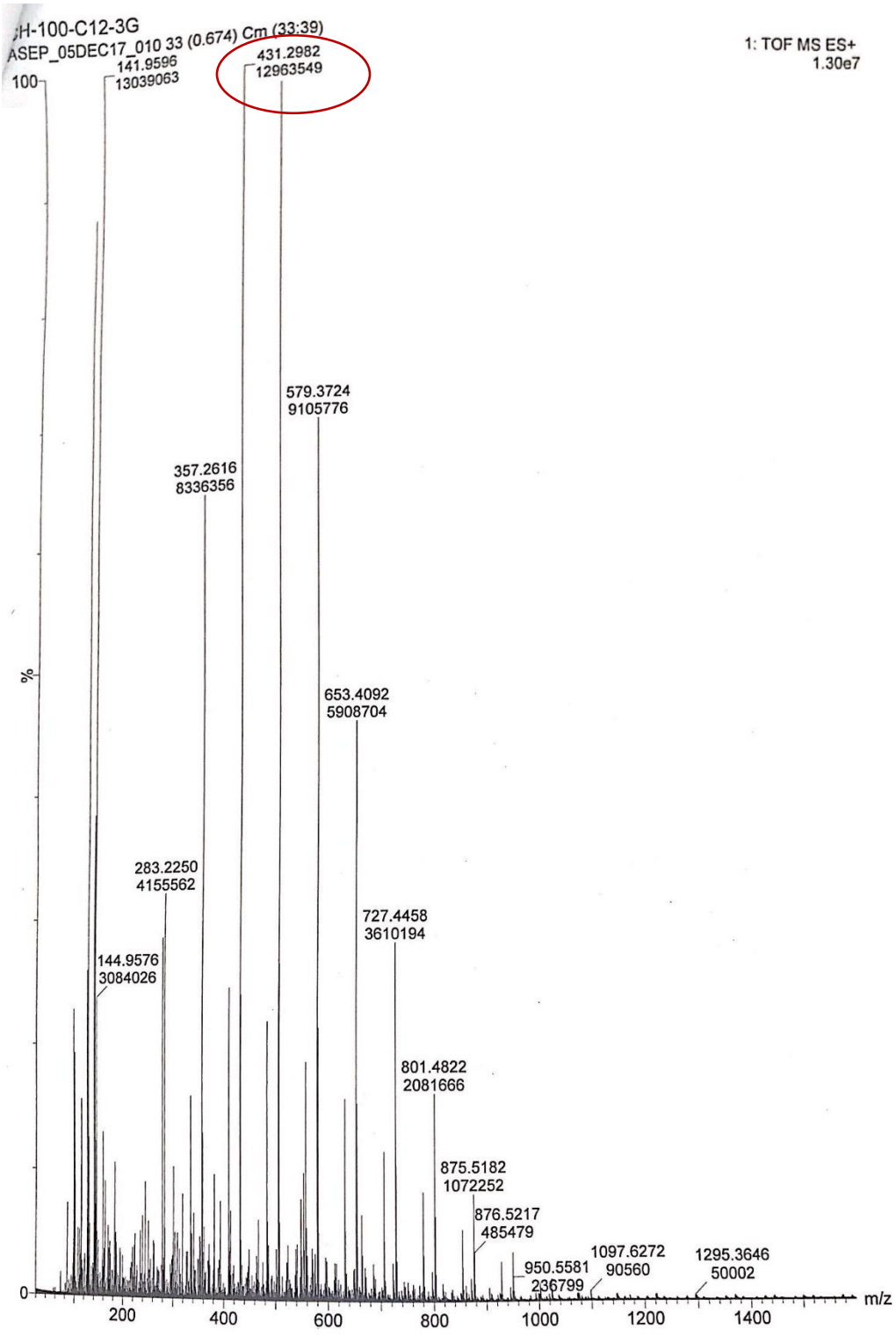


Figure 52 Mass spectrometry result of C_{12}-3G (Na^+)

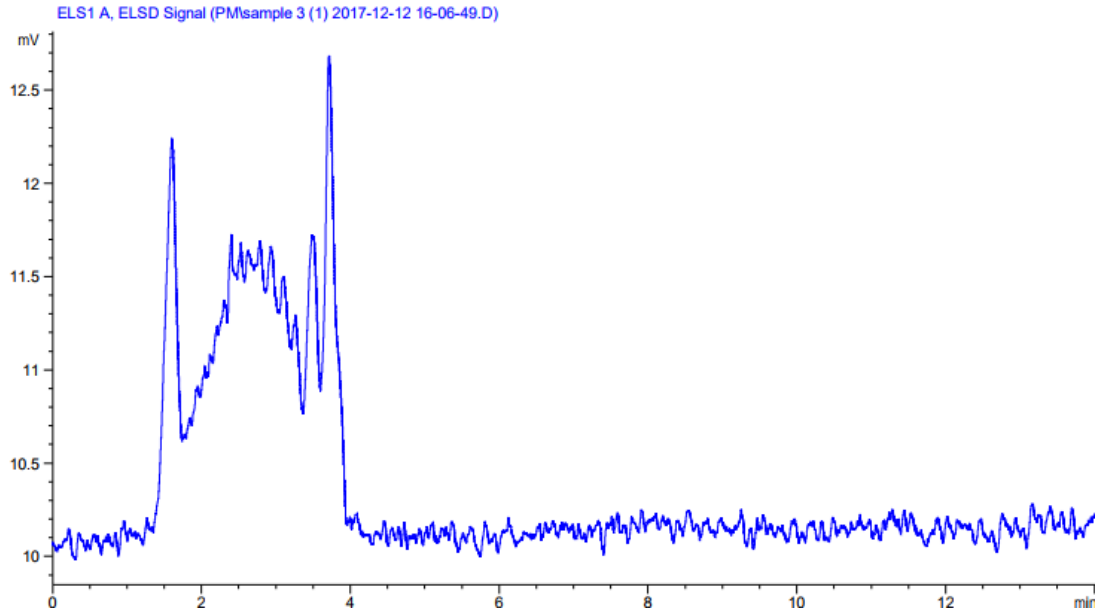


Figure 53 HPLC result of C_{12}-3G (1 mg/m in Methanol)

In Figure 53, the HPLC also shows that there are some other compounds in product. According to all the analysis above, the NMR and MS show that the expected product can be obtained but HPLC shows the polymer is not in high purity. Because the product is a mix of polymer, the conclusion is that expected products can be gotten as main products in reasonable purity.

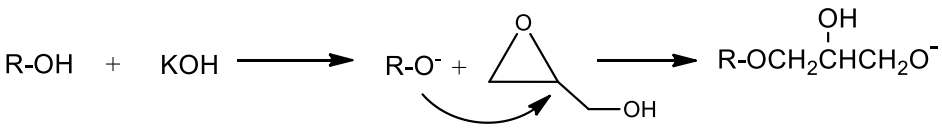


Figure 54 The reaction mechanism of synthesis of poly(glyceryl) ethers using base catalyst

As shown in Figure 54, the reaction mechanism of synthesis of poly(glyceryl) ethers is divided into three steps: first, a small amount of KOH reacts with the starting agent to form an alkoxy anion; then, the alkoxy anion reacts with glycidol monomer to form an active alkoxy anionic. The final alkoxyl anion activity center continues to react with glycidol to complete the chain growth to obtain poly ethers.

Table 17 Reactions for catalyst optimizing of polyglyceryl ethers

Surfactant	FA amount (g)	FA amount (mmol)	EP amount (g)	EP amount (mmol)	Catalyst	Cat. Amount (g)	Reaction
C_{12}-3G	2.48	13.9	2.96	40	No	--	×
C_{12}-3G	2.48	13.9	2.96	40	Amberlyst 15	1	×
C_{12}-3G	2.48	13.9	2.96	40	Amberlyst 15	0.1	×
C_{12}-6G	7.44	39.9	17.76	239.7	$FeCl_3$	0.2	×
C_8-6G	2.93	22.5	10	135	$FeCl_3$	0.2	×
C_{12}-3G	9.92	53.2	11.84	159.8	$La(OTf)_3$	0.3	√
C_{12}-6G	7.44	39.9	17.76	239.7	$La(OTf)_3$	0.3	√
C_{12}-3G	9.92	53.2	11.84	159.8	KOH	0.3	√
C_{12}-6G	7.44	39.9	17.76	239.7	KOH	0.3	√

Judging from the ^{1}H-NMR spectra and the aspect of the final products, $La(OTf)_3$ or KOH can both offer a reasonable purity and high yield. The reaction looks to work better when an acid catalyst such as $La(OTf)_3$ is used rather than when a basic catalyst is, as much less polymerization is observed. Here, partially due to the higher costs of the lanthanum catalyst, most of the reactions were carried out with KOH as catalyst.

4.3.2 The results of synthesis of poly(glyceryl)ether derivatives from glycidol with alcohols

The products are all pale yellow (similar to the AEO commercial products). It is seen that the products are pure enough as the purity is high shown in ^{1}H-NMR (C_8-12G as an example).

Figure 55 shows the result of C_8-12G in ^{1}H NMR (300 MHz, DMSO) δ: 4.46 (s, 13H), 3.48 (m, 62H), 1.55 – 1.14 (m, 12H), 0.85 (t, J = 6.6 Hz, 3H).

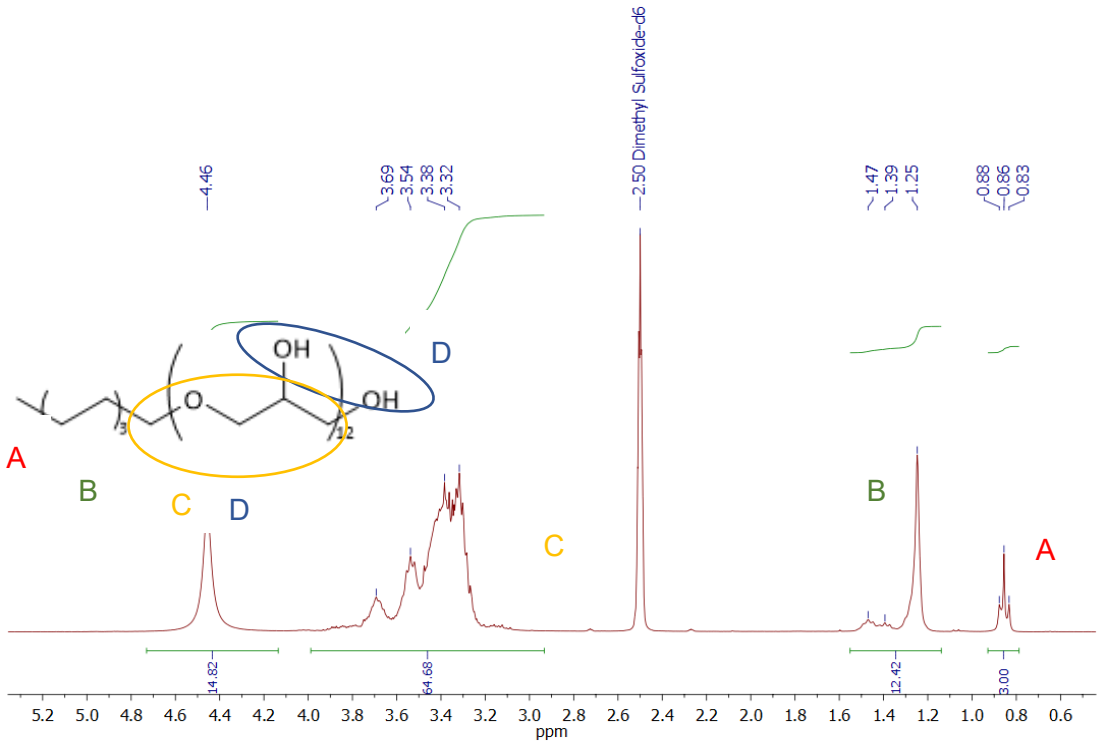


Figure 55 ^{1}H-NMR spectrum (dmso-d6) of C_8-12G

The spectra of ^{13}C-NMR, MS and HPLC show that most of the products can be obtained as main products even though there are some by-products produced with different ratios of glyceryl units. However, with the ratios of glycidol as reactant increasing, expected structure of products are harder to be obtained. For example, for C_{10}-6G (Figure 56), C_{10}-5G and C_{10}-6G can be produced as main products

according to the result of MS but for C_{10}-9G (Figure 57), C_{10}-7G were produced as main product. But the purity is much higher than that in nonylphenol glyceryl ethers. For 3G and 6G products, reasonable products can be obtained.

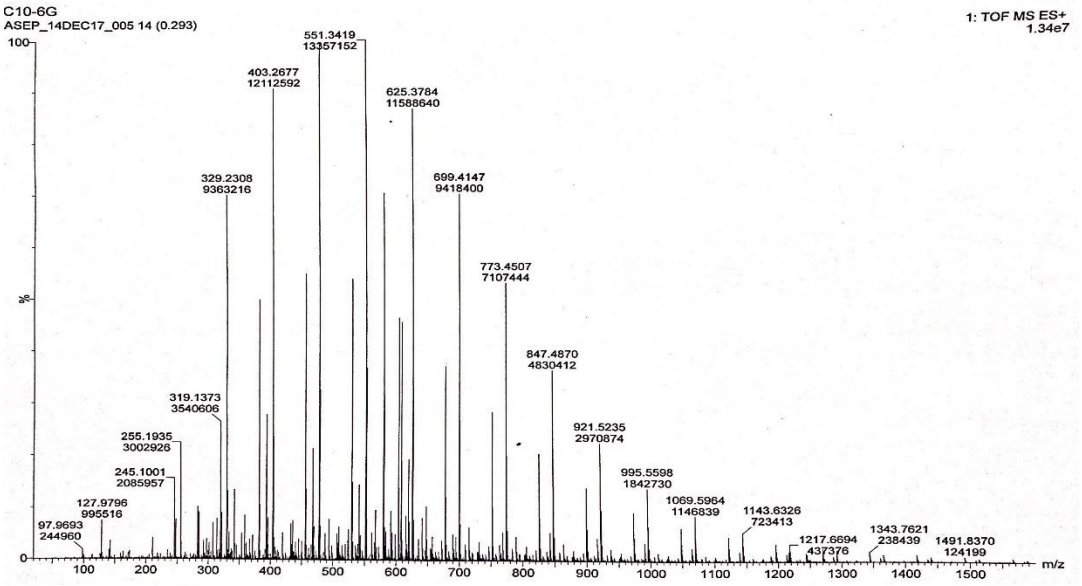


Figure 56 Mass spectrometry result of C_{10}-6G (Na^+)

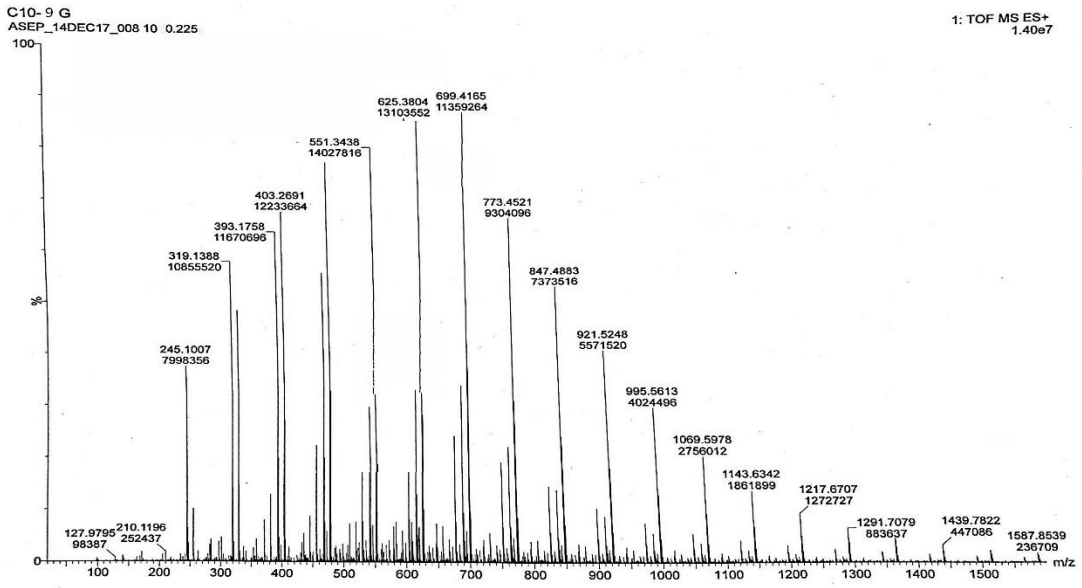


Figure 57 Mass spectrometry result of C_{10}-9G (Na^+)

The melting points of all the polymers are apparently lower than the alky glyceryl

ethers for most of them can be stirred under the room temperature (calculated by ChemDraw). For example, melting point of C_8-3G is 272.67 °C. Comparing 68.95 °C of C_8-1G, it can be seen that the theoretical melting points moved up with the hydrophilic group getting bigger. Besides, they show better water solubility and foaming ability than alky glyceryl ethers. The property test results are shown below.

The disadvantage of this reaction is the long reaction time for the high active glycidol being dropped slowly by injection syringe and it would take hours to get the quantitative products. But its advantages are outstanding, such as the simple reaction operation at just 90 °C, the use of a cheap catalyst and easy purification steps, making it more suitable for economical production.

4.3.3 Properties of Poly(glyceryl)ethers

4.3.3.1 CMC of polyglyceryl ethers

Polyglyceryl ethers were synthesised with the aim of achieving non-ionic surfactants with high hydrophilicity and water solubility. So theoretically, the long hydrophilic group would increase the solubility of the polyglyceryl ethers, which would be particularly beneficial for the products with long carbon chains (≥C_{12}).

Similar to the alkyl glyceryl ethers, the CMC of polyglyceryl ethers decreases with the growth of lipophilic group, that the CMC of C_6-3G is 47.204 g/l and the CMC of C_8-3G is 2.762 g/l while CMC of C_{10}-3G is 0.363 g/l (Table 18). The reason is that a longer carbon chain can increase the insolubility of surfactant in water and makes them easier to form micelles. On the other hand, a larger hydrophilic head has also an influence on the surfactant properties by increasing the CMC of the compound. This phenomenon occurs as a major number of both ether bonds and hydroxyl groups increases the interaction between surfactant molecules and water to form more hydrogen bonds, making it more difficult to create micelles, and therefore, increasing

the CMC. When compared with the effect of lipophilic group, the influence of the hydrophilic one is weaker.

The CMC of C_6-3G is much higher (47.204 g/l) than others because of its short lipophilic group, leading to a high hydrophilicity. In the modern industry manufacturing, the NIS products from hexyl alcohol are not common for their lipophilic group cannot work like C_8, C_{10} and C_{12}, those frequently-used in industry.

If the alky glyceryl ethers are marked as 1G, and are adding by statistical with other polyglyceryl ethers, there is a trend that comes under observation. As shown in the Figure 58, comparing all the polyglyceryl ethers based on octanol, including the single alkyl glyceryl ether C_8-1G, it can be seen that with the hydrophilic group getting longer, the CMC value rises up gradually and obviously from 1.488 g/L (C_8-1G) to 9.036 g/L (C_8-12G), while the surface tension also goes up from 24.17 to 25.71 mN/m.

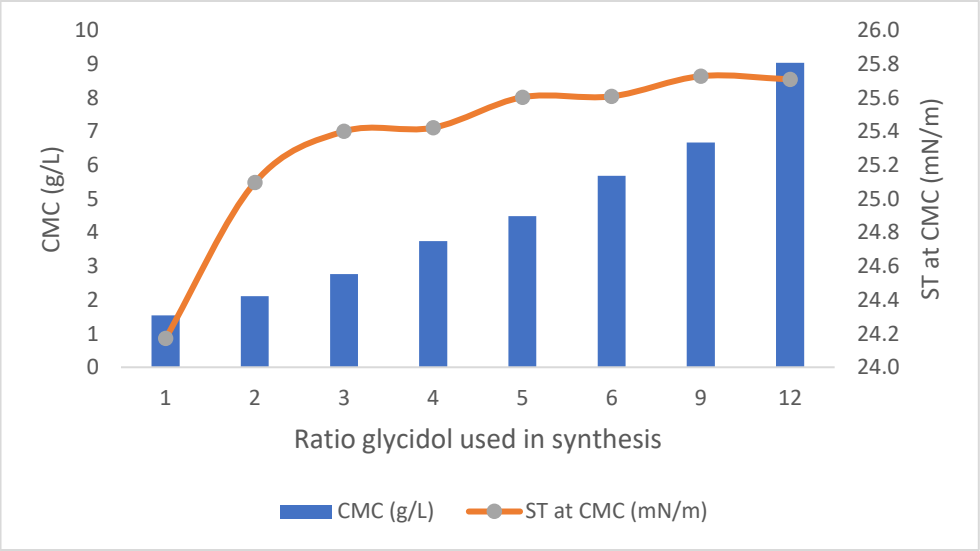


Figure 58 CMC-Glycidol used in synthesis of octanol derivatives

The products from decanol also show this trend as the EP in polyglyceryl ethers increases. As shown in Figure 59, the CMC value rises to 1.426 g/L (C_{10}-12G) from 0.101 g/L (C_{10}-1G), and the surface tension at the CMC from C_{10}-3G to C_{10}-12G increases as well. However, the surface tension of C_{10}-1G is 26.15 mN/m, higher than

C_{10}-3G, 25.20 mN/m. However, C_{10}-1G was found to have a low solubility, and this would cause the surface tension at CMC increasing.

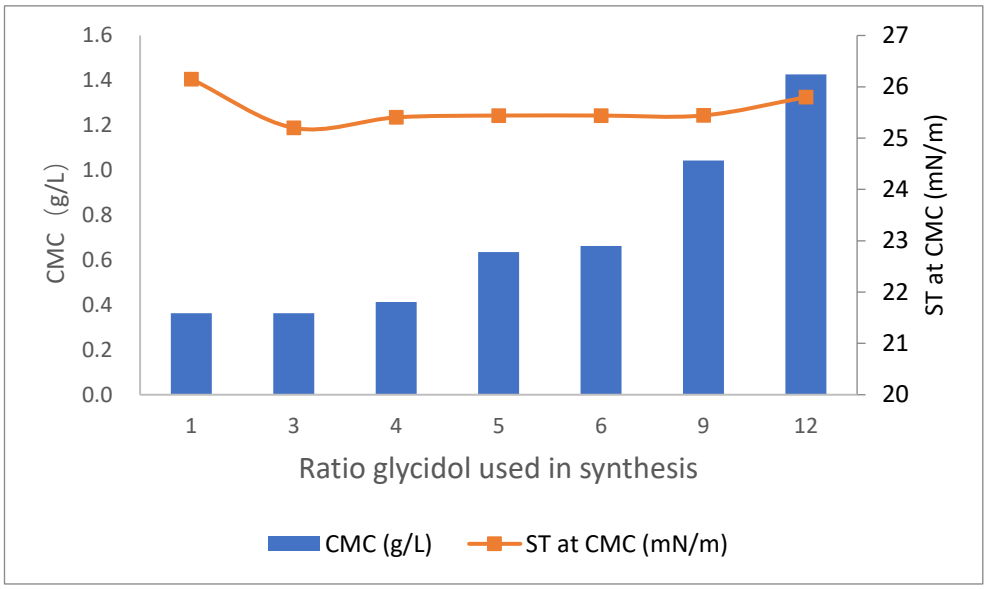


Figure 59 CMC-Glycidol used in synthesis of decanol derivatives

From the comparison of surface tension change with concentration of C_{10} derivatives (Figure 60 60), it can be found that the less glyceryl units in the molecule, the faster the surface tension reduces. In this case, surface tension of C_{10}-3G reduces fastest among C_{10} derivatives and C_{10}-12G reduces slowest. Derivatives of C_8 and C_{12} are in the same condition.

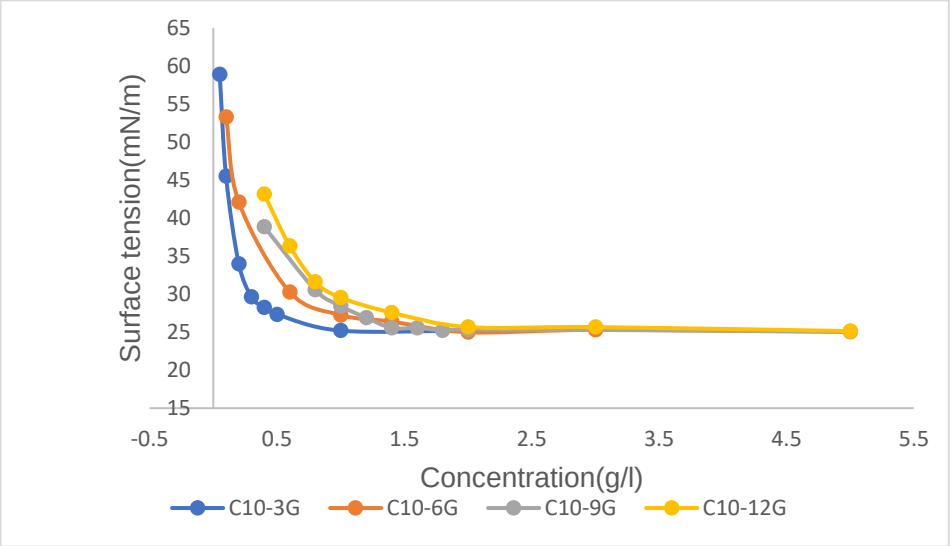


Figure 60 The comparison of surface tension change with concentration of C_{10} derivatives

During the CMC tests of products of dodecanol, the surface tension increase at the CMC caused by insolubility also exists, that the surface tension of C_{12}-3G is 32.89 mN/m, and surface tension of C_{12}-6G is 27.41 mN/m, all higher than C_{12}-9G, 26.89 mN/m, as shown in Figure 61. But the CMC value still follows the trend, increasing with the ratio of EP increasing in the synthesis.

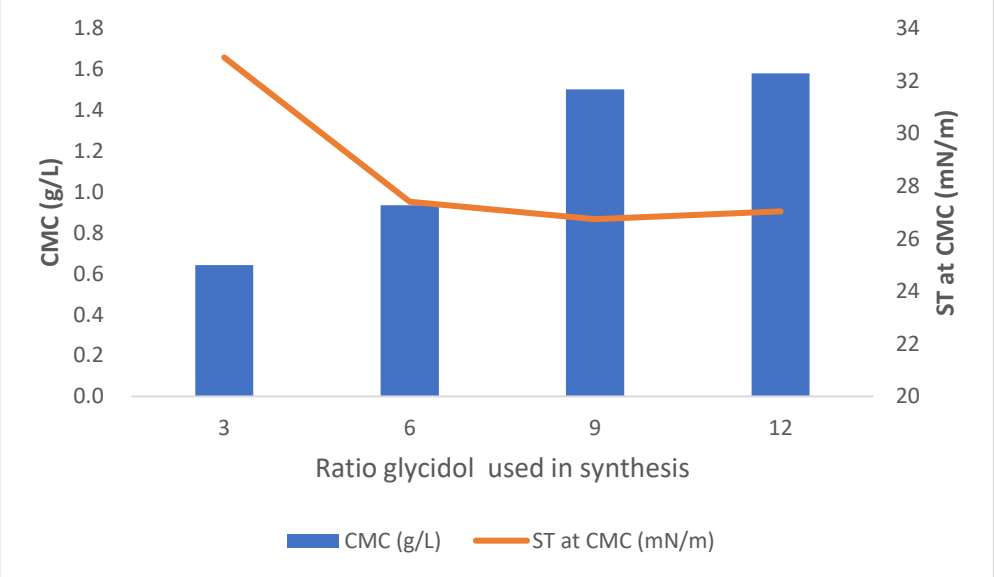


Figure 61 CMC-Glycidol used in synthesis of dodecanol derivatives

Regarding the polyglyceryl ethers with longer carbon chains (≥C_{14}), it was expected

that their CMC values would be lower but unfortunately again, the maximum solubility of the surfactants in water was at lower concentrations than the CMC value, which was not observed. It has previously been reported that large non-ionic surfactants containing propylene oxide and butylene oxide units exhibit behavior which is not related to their composition or HLB, and in those cases HLB values have to be determined experimentally.

Table 18 CMC and HLB of polyglyceryl ethers

Surfactant	Mw (g/mol)	CMC (g/L)	CMC (mmol/L)	Temp (°C)	ST at CMC (mN/m)	HLB value
C_6-3G	324.4	47.204	145.51	24.7	24.86	11.4
C_8-2G	278.4	2.113	7.59	25.2	25.10	8.7
C_8-3G	352.5	2.762	7.84	24.2	25.40	10.4
C_8-4G	426.5	3.744	8.78	25.8	25.42	12.2
C_8-5G	500.6	4.486	8.96	24.8	25.60	14
C_8-6G	574.7	5.679	9.88	24.3	25.61	15.8
C_8-9G	796.9	6.669	8.37	24.3	25.73	>20
C_8-12G	1019.2	9.036	8.87	24.1	25.71	>20
C_{10}-3G	376.5	0.363	0.96	24.0	25.20	9.5
C_{10}-4G	450.6	0.413	0.92	24.4	25.40	11.2
C_{10}-5G	524.6	0.635	1.21	24.2	25.44	13
C_{10}-6G	598.7	0.662	1.11	24.0	25.44	14.8
C_{10}-9G	820.9	1.043	1.27	24.8	25.44	19.2
C_{10}-12G	1043.2	1.426	1.37	25.3	25.80	>20
C_{12}-3G	400.5	0.642	1.57	23.7	32.89	8.5

C_{12}-6G	622.7	0.935	1.50	24.3	27.41	13.8
C_{12}-9G	844.9	1.563	1.85	25.8	26.89	18.2
C_{12}-12G	1067.2	1.633	1.00	24.7	26.87	>20
C_{14}-6G	424.5	Water insoluble				12.8
C_{14}-9G	646.7	Water insoluble				17.2
C_{14}-12G	869.0	Water insoluble				>20
C_{16}-6G	448.5	Water insoluble				11.8
C_{16}-9G	670.8	Water insoluble				16.2
C_{16}-12G	893.0	Water insoluble				>20
C_{18}-9G	694.8	Water insoluble				15.2
C_{18}-12G	917.0	Water insoluble				>20

When comparing polyglyceryl ethers with same length of hydrophilic head but with different length of lipophilic chain, it was found that they also follow the trend observed for single glycidol products. As mentioned before, longer lipophilic chains cause a decrease on the CMC value, as observed between C_8 and C_{10} derivatives, where the CMC values are reduced by one order of magnitude. When in contact with water, short lipophilic chains are stretched requiring more free energy to form micelles and this results in a relatively high CMC value. On the other hand, when the chain is long enough to exceed the equilibrium distance of electrostatic repulsion, it can bend which decreasing the free energy and results in a lower CMC value. However, the increase of the lipophilic chain means that the solubility of the compound in water is reduced, in many cases with the maximum solubility being beyond the CMC. For this reason, the CMCs of the dodecanol derivatives with less than three glyceryl ether units and all the products of tetradecanol, hexadecanol and octadecanol couldn't be tested in this research.

C_{12}-1G was not soluble enough to determine a value for the CMC. However, C_{12}-6G showed outstanding solubility and CMC could be measured easily, which was expected that molecules with longer lipophilic chains but with higher hydrophilic heads, such as C_{14}-12G would be measurable due to its high HLB value. Many of them actually show good solubility as they have very long hydrophilic heads but because of this, it would also lead to a higher CMC value than its maximum solubility, so that its CMC still cannot be measured. Besides, this raises a question about the balance of polyglyceryl ethers between CMC and solubility in water caused by different carbon chain and number of EP units.

C_{12}-3G and the derivatives of C_{14} cannot be tested accurately because they are not soluble enough in water for CMC test. C_{14}-12G have good solubility in water (HLB 18.2) but its maximum saturated concentration is lower than its potential CMC (Surface tension is 35 mN/m at 3 g/l and is still reducing but the solution starts to be cloudy) and it needs to be measured by other methods. For now, the best product according to CMC value is 1-*o*-decylglycerol, but for higher solubility, the polyglyceryl ethers from decanol with longer hydrophilic groups should be chosen.

Comparing all the results in Table 19, the reduced surface tension Π_{cmc}s of all polyglyceryl ethers are from 39.33 to 47.21 $mN \cdot m^{-1}$, most of which are around 46 $mN \cdot m^{-1}$ and the maximum surface excess concentration, Γ_{max}s are as high as 10 μmol/m², which means they are also very closely spaced in the surface, and the minimum area A_{min}s are around 10^{-2} $m^2/\mu mol$. They also follow the trend that the lower A_{min} can make Γ_{max} value be higher. A_{min} of C_6-3G is very low due to its small molecule diameter.

The γ_{cmc} increases when the number of glyceryl units in the polyglyceryl ether surfactants increases. However, the value of A_{min} does not follow the increasing trend with the number of EP units increasing as seen in nonyl phenol surfactants, which indicates that in the air/water interface there may be some molecules folding or the

different molecule structures have some influence on molecular arrangement in the air/water interface.

Table 19 Surface properties of polyglyceryl ethers

Surfactant	CMC (mmol/L)	Temp (°C)	γ_0 (mN·m^{-1})	γ_{cmc} (mN·m^{-1})	Π_{cmc} (mN·m^{-1})	Γmax (μmol/m^2)	Amin (A^2)
C_6-3G	145.51	24.7	72.07	24.86	47.21	31.870	0.005
C_8-2G	7.59	25.2	71.99	25.1	46.89	17.611	0.009
C_8-3G	7.84	24.2	72.15	25.4	46.75	14.272	0.012
C_8-4G	8.78	25.8	71.90	25.42	46.48	18.257	0.009
C_8-5G	8.96	24.8	72.05	25.6	46.45	13.774	0.012
C_8-6G	9.88	24.3	72.13	25.61	46.52	17.465	0.010
C_8-9G	8.37	24.3	72.13	25.73	46.40	14.905	0.011
C_8-12G	8.87	24.1	72.16	25.71	46.45	17.057	0.010
C_{10}-3G	0.96	24	72.18	25.2	46.98	16.508	0.010
C_{10}-4G	0.92	24.4	72.12	25.4	46.72	10.131	0.016
C_{10}-5G	1.21	24.2	72.15	25.44	46.71	16.370	0.010
C_{10}-6G	1.11	24	72.18	25.44	46.74	7.187	0.023
C_{10}-9G	1.27	24.8	72.05	25.44	46.61	5.575	0.030
C_{10}-12G	1.37	25.3	71.97	25.8	46.17	8.576	0.019
C_{12}-3G	1.57	23.7	72.22	32.89	39.33	14.950	0.011
C_{12}-6G	1.5	24.3	72.13	27.41	44.72	17.950	0.009
C_{12}-9G	1.85	25.8	71.90	26.89	45.01	12.215	0.014
C_{12}-12G	1.00	24.7	72.07	26.87	45.20	9.169	0.018

4.3.3.2 Comparison with the commercial products

As indicated previously, the CMCs of all the polyglyceryl ethers samples (C_8 to C_{12}) are lower than 10 mmol/L, which are very close to CMC of similar non-ionic surfactants (Table 20).

Table 20 CMC of some similar NIS (AEO)[114]

Compound	Temp(°C)	Log CMC	CMC(mmol/l)
C_8EO5	25	−2.11 mol/l	7.76
C_{10}EO5	25	−3.11 mol/l	0.776
C_{10}EO8	25	-2.98 mol/l	1.05
C_{12}EO4	25	−4.19 mol/l	0.087
C_{12}EO8	25	−3.95 mol/l	0.112

As mentioned before, the CMC of ionic surfactants is much higher than the CMC of non-ionic surfactants because the hydrophobic groups of the ionic surfactants have a stronger hydration effect with water, and the hydrophilic groups of the non-ionic surfactants have a lower hydrophilicity. Similarly, the increasing of number of -OH groups in the NIS molecules would also increase hydrophilicity, leading to the increase of CMC value.

Compared with other types of surfactants, the CMC values of these compounds are lower because non-ionic surfactants do not apply ions in water and easier to form micelles (Table 21). It can be seen that for different type of surfactants (even non-ionic surfactants), their magnitudes are different. Low CMC values means this kind of aqueous solution is easy to achieve a balance while high CMC means this surfactant aqueous solution is not easy to collect micelles then it can be used in detergency for that the surfactant concentration is lower than CMC, without micelles.

Table 21 CMC of some other types of surfactants

Compound	Temp (°C)	CMC (mmol/l)
Hexadecyl trimethyl ammonium chloride	25	16.0
Sodium octyl sulfonate	25	150.0
Sodium octyl sulfate	40	136.0
Sodium lauryl sulfate	40	8.60
Tetradecyl sulfate	40	2.40
Lauric acid potassium	25	12.50
Sodium dodecyl sulfonate	25	9.00

According to Table 22 that are collected from reference papers,[115] the CMC of my products synthesized here are higher than theirs which indicates the synthesized products have strong effect on surface tension reduce among NIS. In addition, my A_{min} values are higher than theirs, so my products are more closely packed.

Table 22 Surface Activities of Aqueous Solutions of C_{12}Eon (similar products) at 25 °C

Compound	Mol. Weight (g/mol)	CMC (mmol/L)	γ_{CMC} (mN/m)	Γ_{max} (μmol/m^2)	A_{min} (A^2)
C_{12}EO4	362	0.065	35.2	360	0.0046
C_{12}EO6	450	0.087	38.5	310	0.0054
C_{12}EO8	538	0.112	41	250	0.0066

There are several factors that must be noted:

1) The ability of a surfactant to form micelles is not only related to its HLB value, but also to its three-dimensional structure. As such, molecules with similar CMC and calculated HLB values can display very different experimental HLB values and solubilities, depending on the branching degree of the surfactant.

2) Surfactants often contain small amounts of unreacted raw materials, as well as other additives and electrolytes, which may have a great impact on the CMC surfactant system.

For example, the addition of salt to the surfactant solution can reduce the critical micelle concentration. The addition of salt can promote the formation of micelles of surfactants, reducing the critical micelle concentration. It is clear that this is because the counter ion is adsorbed on the polar group of the surfactant in the micelle, reducing the repulsive force between the polar groups facilitating micelles formation.[116]

The alcohol that was not been removed completely in the purification also has influence on CMC values. The effect of alcohol on the CMC of surfactants is complex, but generally CMC decreases with the increase of the amount of alcohol, and the degree of reduction is related to the structure of the alcohol. For the fatty alcohols, the ability of reducing CMC would increase with the increase of the hydrocarbon chain. The reason is that alcohol molecules can penetrate into the micelles to form mixed micelles, which can reduce the repulsive force between the surfactants and increase the entropy of the system due to the addition of alcohol molecules, so the micelles tend to form and increase easier.

Table 23 Library of potential applications for poly(glycerol) ether surfactants (according to their HLB values).

Surfactant	Potential use
C_6-3G	Emulsifier
C_8-1G	wetting agent, water-in-oil emulsions.
C_8-2G	wetting agent, water-in-oil emulsions.
C_8-3G	oil-in-water emulsions, detergents and cleansing agents.
C_8-4G	oil-in-water emulsions, detergents and cleansing agents.
C_8-5G	oil-in-water emulsions, detergents and cleansing agents.
C_8-6G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_8-9G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_8-12G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{10}-1G	water-in-oil emulsions, co-emulsifier
C_{10}-3G	wetting agent, water-in-oil emulsions.
C_{10}-4G	oil-in-water emulsions, detergents and cleansing agents.
C_{10}-5G	oil-in-water emulsions, detergents and cleansing agents.
C_{10}-6G	oil-in-water emulsions, detergents and cleansing agents.
C_{10}-9G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{10}-12G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{12}-3G	wetting agent, water-in-oil emulsions.
C_{12}-6G	oil-in-water emulsions, detergents and cleansing agents.
C_{12}-9G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{12}-12G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{14}-6G	oil-in-water emulsions, detergents and cleansing agents.
C_{14}-9G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{14}-12G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{16}-6G	oil-in-water emulsions, detergents and cleansing agents.
C_{16}-9G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{16}-12G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{18}-9G	detergent, wetting agent, emulsifier, foaming agent, dispersant.
C_{18}-12G	detergent, wetting agent, emulsifier, foaming agent, dispersant.

4.3.3.3 Foaming abilities of poly(glyceryl)ethers

As a rule of thumb, all the synthesized polyglyceryl ethers shown better solubility and foaming ability comparing with the alkyl glyceryl ethers. Their foam is all white and dense, and some of them can be stable for several minutes.

As shown in the Figure 62, as the hydrophilic head grows by adding more glyceryl units, the solubility of all C_8 NIS increases and so it does their foam ability until C_8-5G. After this compound, the foaming ability lowers as it is observed. The C_8 products with highest foaming ability are C_8-3G and C_8-5G, with 90 ml of foam after 10 seconds of shaking the respective products in the cylinder. However, C_8-4G has shown much lower foam even though this measure was repeated several times with the same results. Therefore, this anomaly might be worth of further study but unfortunately this would require an in-depth investigation which is not the object of this work.

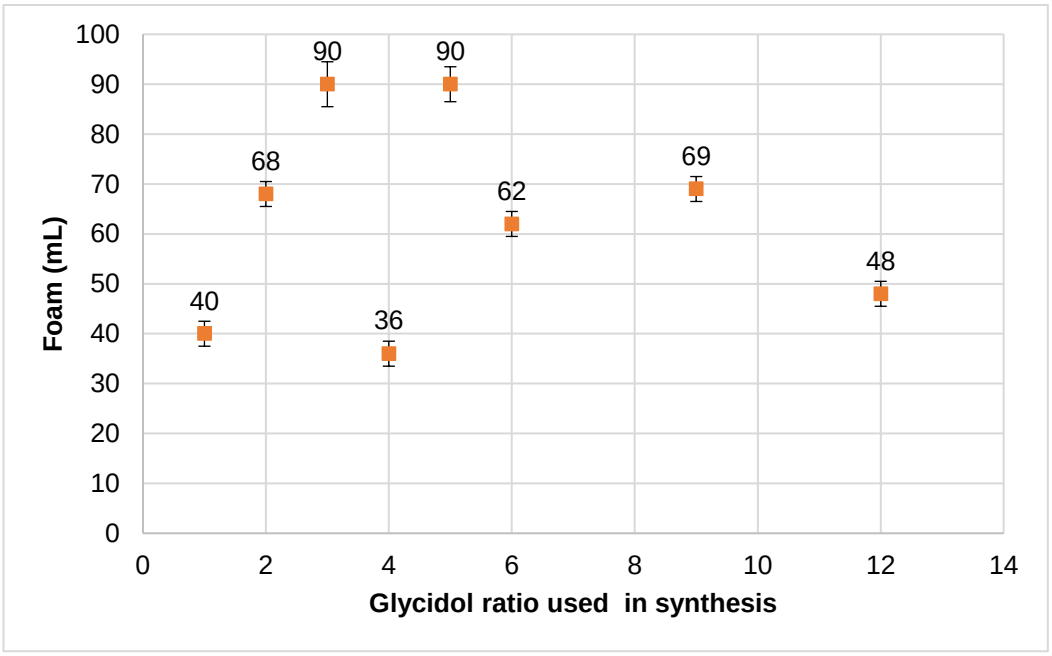


Figure 62 Foaming ability of octanol derivatives

In Figure 63, the C_{10} derivatives show a different foaming tendency to those of C_8 as it rises as EP ratio in synthesis increases and C_{10}-12G shows a very good foaming ability. It is hard to speculate if more EP will lead to an even higher foam volume for the products of C_8 have a decreasing trend after getting foaming peak.

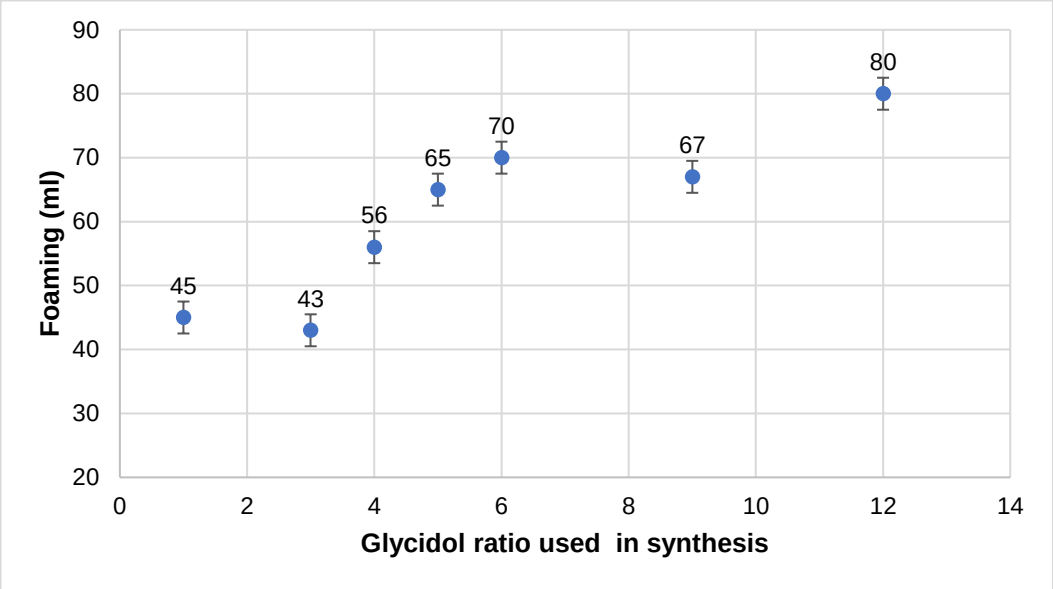


Figure 63 Foaming ability of decanol derivatives

In Figure 64, the polyglyceryl ether products of C_{12} also showed better foaming abilities than 1-o-dodecylglycerol and the foam of these products are very dense. The products of 3G to 12G foamed very similar so combined with the conclution above, it can be conjectured that adding more EP to synthesis products with longer hydrophilic group can result in larger volumes of foam.

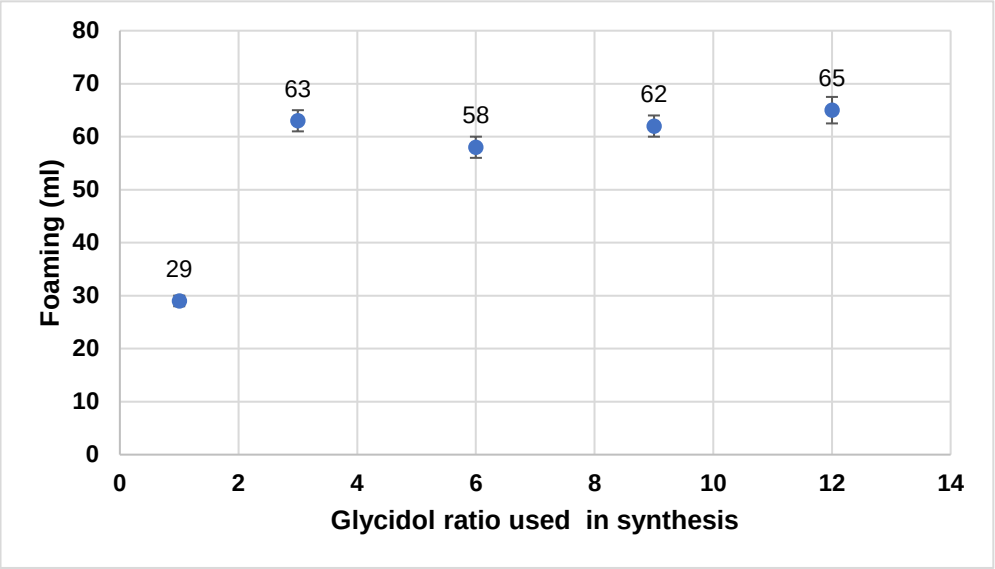


Figure 64 Foaming ability of dodecanol derivatives

The 1-octanol, 1-decanol, 1-dodecanol 1% weight solutions were also tested as C_8-0G, C_{10}-0G and C_{12}-0G but none of them are water-soluble and they cannot foam either.

All the polyglyceryl ethers from tetradecanol, hexadecanol and octadecanol can foam but the foam volumes are low. In contrast to the insoluble alky glyceryl ethers (C_{14} to C_{18}), they can all foam aproximately 40 ml.

The ratio of the height of the foam to the initial foam height at 5 min was measured as a measure of its stability, which is foam expansion. From the Figure 65, it can be seen that at 5 minutes, the foam of C_8-3G gave the highest expansion and the foam of C_{12}-3G was the most stable after 2 minutes.

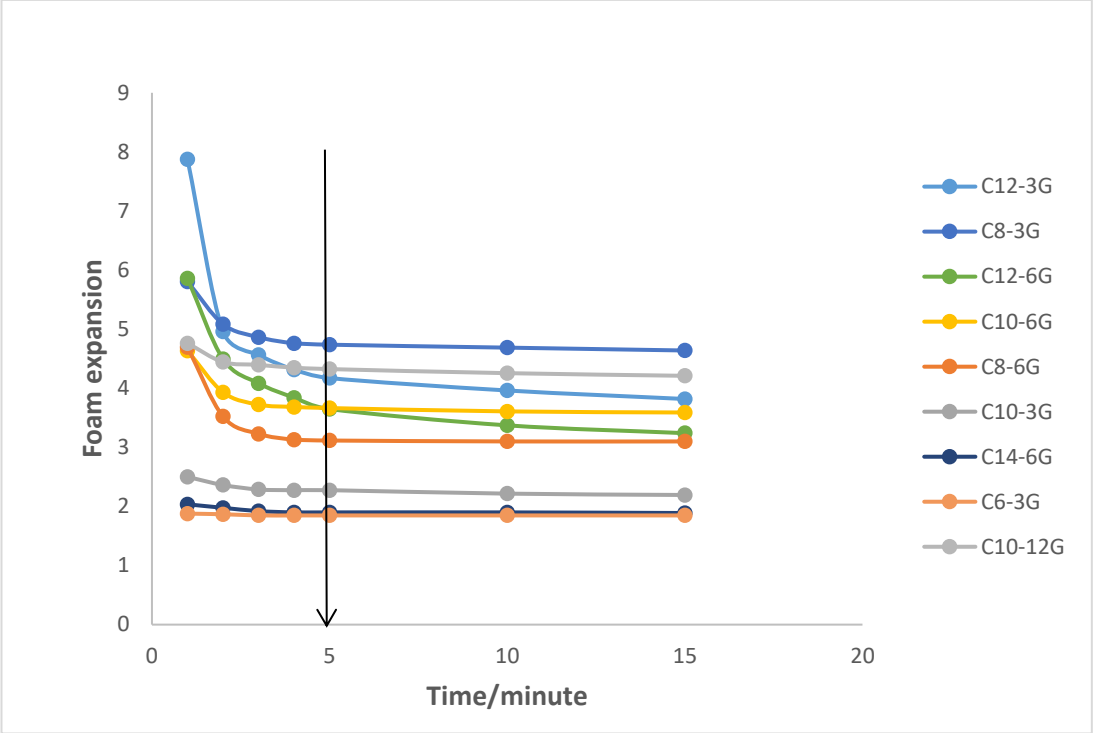


Figure 65 Foaming expansion comparison of polyglyceryl ethers

Experiments about the different concentration aqueous solutions of all products were carried out of foaming test to find out the concentration influence on foam and just like Figure 66 shows, the foam volume would increase as the concentration getting higher, but there must be a limit above which the foam ability of solution would drop.

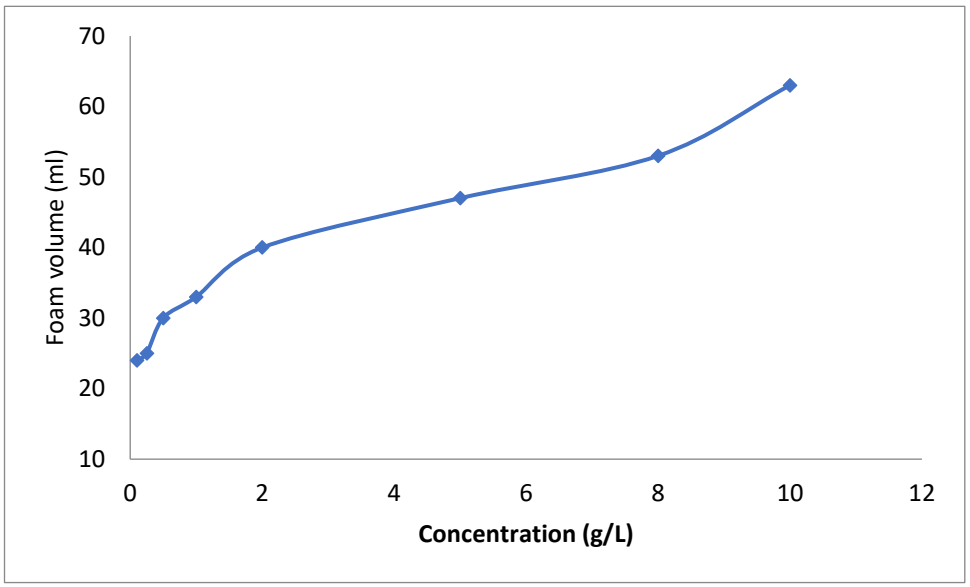


Figure 66 Concentration influence of C_{12}-3G foaming test

The foam is thermodynamically unstable. The reason for the instability is that with the increase in the total surface area of the system after the formation of the foam, the energy is increased, and it will spontaneously go to the direction of energy reduction and the total surface area decreased, that is, the bubble burst. The bursting of the foam is mainly due to the diffusion of gas through the membrane and the flow of the liquid caused by the gravity and the pressure of the points in the liquid film.

The results of surface viscosity experiments and the theory show that the key factor determining the stability of the foam is the strength of the liquid film, and the presence of the surfactant molecules on the surface film increases the surface viscosity and prevents the liquid from flowing out of the membrane, thereby stabilizing the foam.

Polyglyceryl ethers show an excellent foaming performance as non-ionic surfactants among which the one from octanol with three and five EP foam best which are 90 ml after 10 seconds shake. As a comparison, washing liquid which contains a variety of active ingredients, emulsifiers was also tested by the same method and the result is that washing liquid foams 97 ml but the foam of polyglyceryl ether is denser. The results are shown in Table 24.

Table 24 Comparison of washing liquid and part of non-ionic surfactants

Washing liquid		**C_8-3G**		**C_8-5G**	
Volume of liquid (ml)	Foam expansion	Volume of liquid (ml)	Foam expansion	Volume of liquid (ml)	Foam expansion
18.5	5.243	15.5	5.677	17.8	5.056
18.8	5.160	17.7	4.972	19	4.737
18.9	5.132	18.5	4.757	19.2	4.688
18.9	5.132	18.9	4.656	19.3	4.663
19	5.105	19	4.632	19.4	4.639
19	5.105	19.2	4.583	19.7	4.569
19	5.105	19.4	4.536	19.8	4.545
Foam (ml)		Foam (ml)		Foam (ml)	
97		90		90	

It is satisfied that as NIS they can foam similarly to the mixed anionic surfactant which has been put into the market. These products can be improved by mixed with other agents and can be used in the foaming agent industry. By increasing the liquid film to adsorb the surfactant molecules, the liquid film strength is increased and the stability of the foam would increase.

4.4 Cloud Point

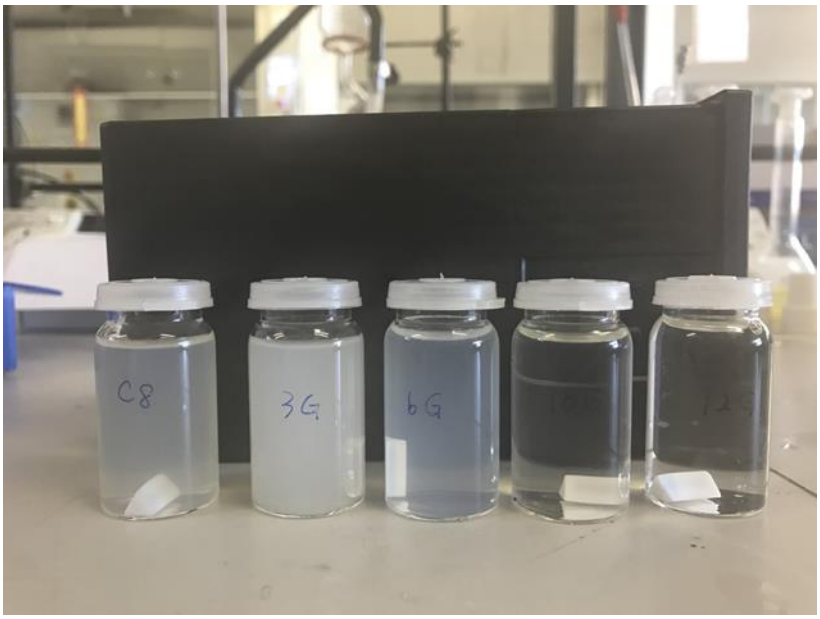


Figure 67 The 1 wt % aqueous solutions of 1-o-octylglycerol, C_9-Φ-G3, G6, G10 and G12 (from left to right)

Unfortunately, all the samples are either clear or cloudy during this temperature period (examples as Figure 67). For those cloudy samples at 1 wt%, they are not soluble enough for cloud point tests, and for the samples which are clear between temperature range of 5-100 °C, their cloud points are determined to be more than 100 °C. Only cloud points of C_6-3G, C_8-9G, C_8-12G, C_9-Φ-G10, C_9-Φ-G12 are over 100 °C, for others, all the solutions except are cloudy and their cloud point cannot be tested here.

For NIS with cloud point above 100 °C, it cannot be measured directly under normal pressure. So there are two methods to estimate the NIS with cloud point above 100 °C. One is the epitaxial method,[117] which is a salting-out based on effect of the electrolyte, under normal pressure to determine the different electrolyte concentration at the cloud point and plot as a function of concentration. The plot can be extrapolated to the concentration of zero, that is, the approximate cloud point value. Variation in measurements should be carried out in different electrolytes to avoid errors. Of course,

this method has some limitations, because under high pressure, whether the relationship of cloud point and the electrolyte concentration is linear or not is unknown. The second is the contrast method, assuming that for a structurally similar NIS, the cloud point change is mainly dependent on the electrolyte species. A non-ionic surfactant (NIS1) with similar structure of the NIS to be tested is chosen to measure the cloud point change of a solution containing the salting-out electrolyte. Then the cloud point of NIS1 needs to be less than 100 °C at an atmospheric pressure. Then the cloud point of the NIS at the same concentration of electrolyte is tested. Then the different between these two is added to the cloud point of the NIS1 with no electrolyte present to get the approximate NIS cloud point. However, these two methods only can obtain approximate value.

4.5 Cleaning Tests

A productive collaboration with Foxgrove Tec Ltd (FXT, Yorkshire, UK) was undertaken in order to measure the detergency of a few of the synthesised non-ionic surfactant products presented in this work. In this company, R&D work is carried out for other companies which actively sell cleaning formulations into the road tanker cleaning market in the UK and Europe. For the time being, their current commercial formulation is based on decanol ethoxylates, especially with 8-9 EO units. it was proposed to testing poly(glyceryl) ether derivatives from decanol with three, six and nine equivalents of glycidol (C_{10}-3G to 9G). 50 grams of each product were shipped to them and the detergency properties of the decanol poly(glyceryl) ethers were tested and they could become potential candidates for cleaning applications.

The dissemination of these results has been agreed with the company. In order to protect sensitive data, the samples will be coded as TS-2001 and Helex-LC.

Test strip preparation

Stainless steel strips (80 x 25 x 2mm) are coated with 3 different latexes supplied by Synthomer ie VV530 (VA/VeoVA/butyl acrylate), R387 (acrylic/styrene copolymer) and D308 (acrylic ester). The strips are then cured over 48 hours.

Cleaning performance

The detergent formulation is added to water at 20% w/w and the solution is heated to 70 °C in a 250-ml beaker using a magnetic bar stirrer. The coated, Stainless steel strips are then suspended in the stirred solution and the degree of latex removal is recorded after 0.5 and 1.5 hours. An average of the removal of the 3 strips at 1.5 hours is also noted.

As observed in Table 25, in the standard formulation TS-2001 -which is known to contain water, phosphate, KOH, MEA and glycol-ether- whilst all the rest of detergents performed well, the 3G mixture was noticeably less effective (60% average clean after 0.5 hours, 70% after 1.5 hours) compared to 6G and 9G and the reference based on commercial XP-90;[118] all gave an average of 80-90% cleaning efficiency after 0.5 hours and 90-100% clean after 1.5 hours.

In the higher pH formulation, Helex-LC, again each surfactant performed well although less so the 3G and 6G products; after 0.5 hours, the average clean was 35-60% compared to those of 9G and XP-90 reference of 80-90%. Similar trends were observed after 1.5 hours, where 60-80% cleaning efficiency was found for 3G and 6G whereas outstanding cleaning efficiencies of 90-100% were achieved for both the 9G product and reference.

In conclusion, all the NIS tested performed well in the standard cleaning tests for latex removal although C_{10}-3G was noticeably less effective in comparison to the rest in both formulations. In the TS-2001 formulation, both 6G and 9G surfactants were similar to the XP-90 reference but in the Helex-LC, only the 9G variation was

comparable to the XP-90 reference, which gives an idea of the direction it's needed to be taken in order to achieve high-performance NIS for this particular application.

Table 25. Results of the cleaning tests of C_{10}-3,6 and 9G and compared against commercial benchmark BASF XP-90.

Formulation	Sample	Cleaning % after 0.5 h				Cleaning % after 1.5 h			
		VV530	R387	D308	Avg.	VV530	R387	D308	Avg.
TS-2001 (Basic pH)	C_{10}-3G	100	90	0	60	100	100	0	70
	C_{10}-6G	100	90	50	80	100	100	80	90
	C_{10}-9G	100	80	50	80	100	100	100	100
	XP-90	90	100	80	90	100	100	100	100
Helex-LC (Very basic pH)	C_{10}-3G	90	50	50	60	100	90	50	80
	C_{10}-6G	100	0	0	35	100	50	20	60
	C_{10}-9G	90	100	70	90	100	100	100	100
	XP-90	100	100	40	80	100	100	60	90

4.6 Synthesis of alkyl glyceryl ethers from GLC with fatty alcohols

As described in patent WO 2013139995 A1, GLC was reacted one hour with linear alcohol (molar ratio 1:4) at 140 °C, under nitrogen condenser in presence of solid acid Amberlyst 35. However, during this research, after the reaction as above, that Figure 68 showed no conversion to product by ^{1}H-NMR shows:^{1}H NMR (300 MHz, CDCl3) δ: 0.88 (t, J = 6.5 Hz, 3H), 1.26 (s, 14H), 1.55 (d, J = 6.4 Hz, 20H), 1.79 - 2.00 (m,

2H), 3.32 - 4.22 (m, 41H). Then KOH as base catalyst was tested but still no product manufactured.

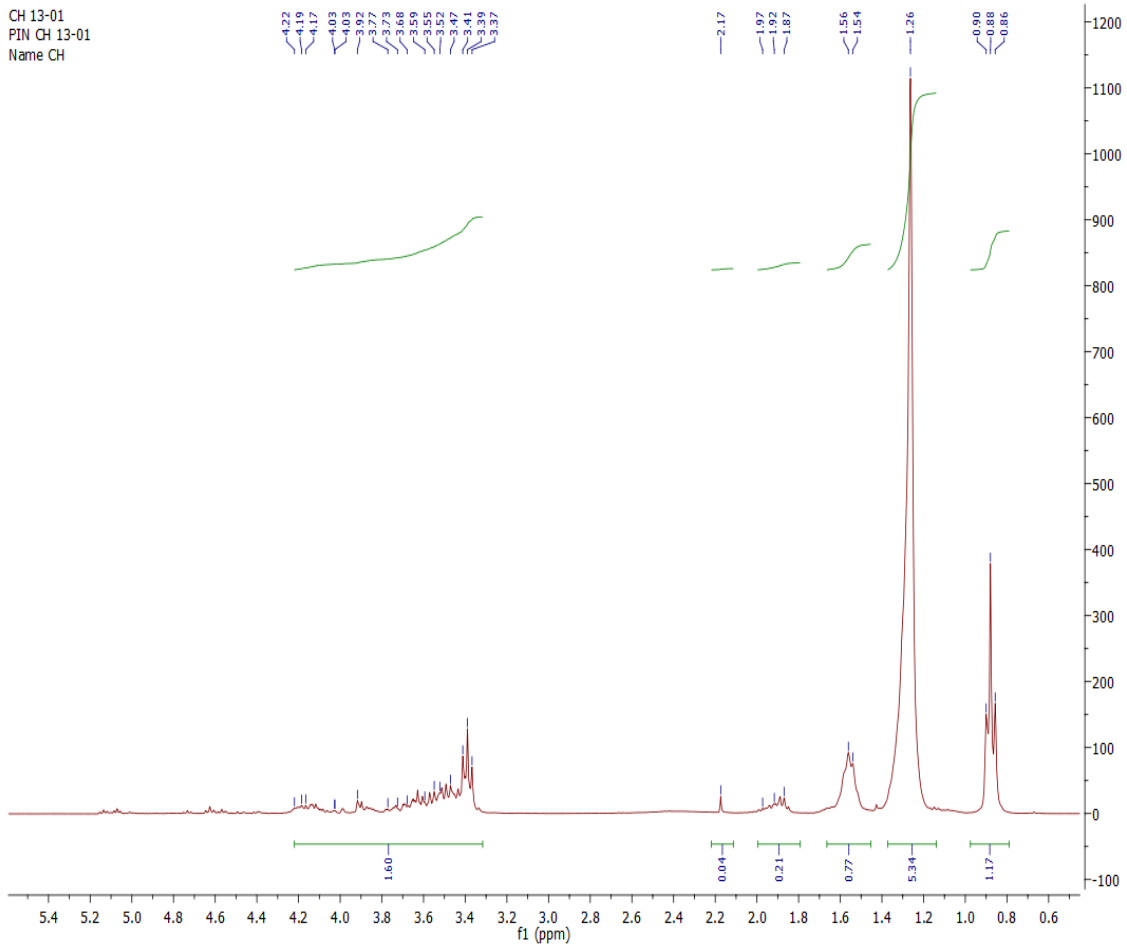


Figure 68 [1]H-NMR of the synthesis of alkyl glyceryl ethers from GLC with decanol using Amberlyst 35 as catalyst

5 Conclusions

Surfactants are widely used in textile, cosmetic and agricultural fields because of their ability to significantly reduce the interfacial tension from 72 mN/m to about 25 mN/m and they are an indispensable chemical agent for many industrial sectors. Among them, non-ionic surfactants are an important class of products. Non-ionic surfactants are emulsifiers, with excellent wetting properties making them useful in detergent applications. Fatty alcohol ethoxylates are the main family of NIS global production. They are currently produced by addition of ethylene oxide, a highly toxic and flammable gas, to the fatty alcohol. Therefore, in this project, another epoxide, glycidol is proposed as an alternative to synthesize high-quality NIS using green production methods.

Three main families of compounds have been synthesized and characterized: glyceryl ethers from fatty alcohols, nonylphenol poly(glycerol) ethers and poly(glycerol) ethers from fatty alcohols, in which varying hydrophilic groups length poly(glycerol) ethers are new for the market. They are synthesized in different ways and have been analyzed by ^{1}H-NMR, ^{13}C-NMR, MS and HPLC. The CMCs, cloud points and foamability of all the synthesized surfactants have been determined, when possible (good solubility in water is essential).

Regarding the synthesis of materials, the results were generally similar with acid catalysts such as $La(OTf)_3$ is used or basic catalysts, all showed high conversion in synthesis of poly NIS. KOH was selected as the preferred catalyst based on cost and ease of commercialization.

The purity of nonylphenol poly(glycerol) ethers and poly(glycerol) ethers products is not very high as there are many by-products produced with different ratios of glyceryl units. This phenomenon is more obvious with the ratio of glycidol in synthesis increasing.

Most of the glyceryl ethers showed very low solubility in water, especially those where the alkyl chain contained 12 or more carbons. For the water soluble (e.g. C_8-C_{10} alcohols), their CMCs are not very high, and their surface tension was very low. Due to their lipophilicity, they can be used as defoaming agents, dispersants for solids in oil or co-emulsifiers.

Octyl- and nonylphenol poly(glycerol) ethers are very promising NIS for they behaved well in CMC test and showed good solubility. Their CMCs are relatively low and comparable to those of analogous commercial ethoxylate products and their foamability is quite good. However, their melt points are high - they are solid in room temperature. They can be used as detergents, solubilizers and cleansing agents.

Poly(glycerol) ethers were synthesized in order to increase the polarity of glyceryl ethers by adding different amounts of glycidol to the alkyl chain to expand the hydrophilic group. The results obtained for C_8-C_{12} derivatives were good, with also relatively low CMC values, very low surface tension (generally around 25 mN/m) and moderate foamabilities. C_{14} and longer carbon chain derivatives behave better in the aqueous solution than the product with single EP, but their limited solubility in water made it difficult to determine their main surfactant properties even after the addition of twelve glyceryl groups.

Three of my synthesized surfactants (C_{10}-3,6 and 9G) have been recently tested in Foxtrot Tec Ltd (England) as main active detergents in cleaning formulations to remove latexes and resins from road tankers. All our surfactants formulated well into the standard KC-Tech mixtures and performed well in the standard cleaning tests for latex removal although the 3G was noticeably less effective. In the standard formulation, the 6G and 9G surfactants were similar to the XP-90 reference but in the basic pH formulations, only the 9G variation was comparable to the XP-90.

6 Appendix

Materials

Glycidol	>95%, GLT
Hexanol	98%, SIGMA-ALDRICH
Octanol	98%, SIGMA-ALDRICH
Decanol	99%, ALDRICH
Dodecanol	98%, ALDRICH
Tetradecanol	98%, SIGMA-ALDRICH
Hexadecanol	95%, SIGMA-ALDRICH
Octadecanol	95%, ALDRICH
Nonylphenol	Technical grade, mixture of ring and chain isomers, ALDRICH
Cyclohexane	>=97%, SIGMA-ALDRICH
Methanol	99.99%, Fisher scientific UK
Potassium hydroxide	98%, SIGMA-ALDRICH
$La(OTf)_3$	99%, SIGMA-ALDRICH
Iron(III) chloride ($FeCl_3$)	99%, SIGMA-ALDRICH
Magnesium sulfate-dried	Fisher Scientific UK
Amberlyst 36	ALDRICH
Amberlyst 15 hydrogen form	ALDRICH

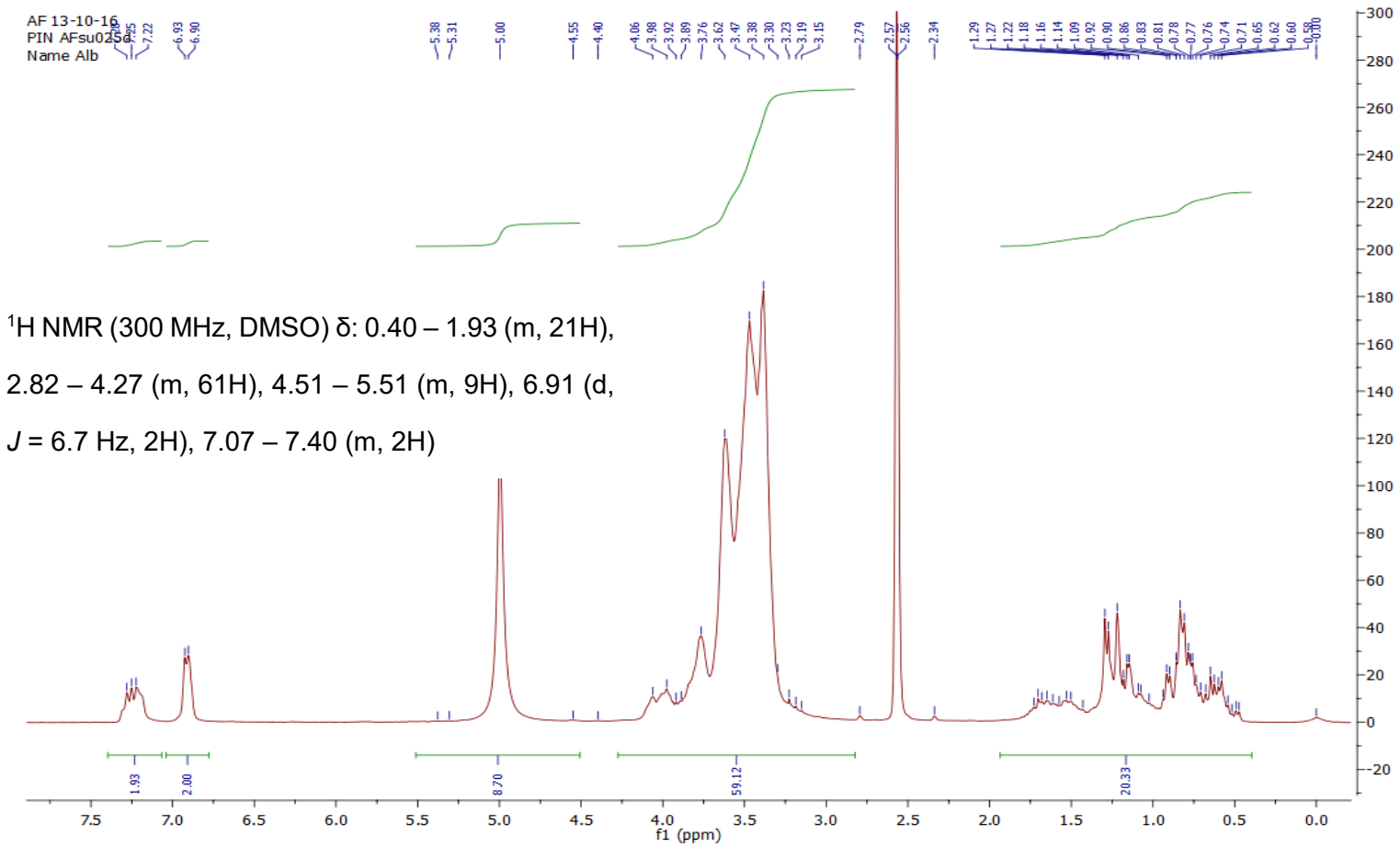
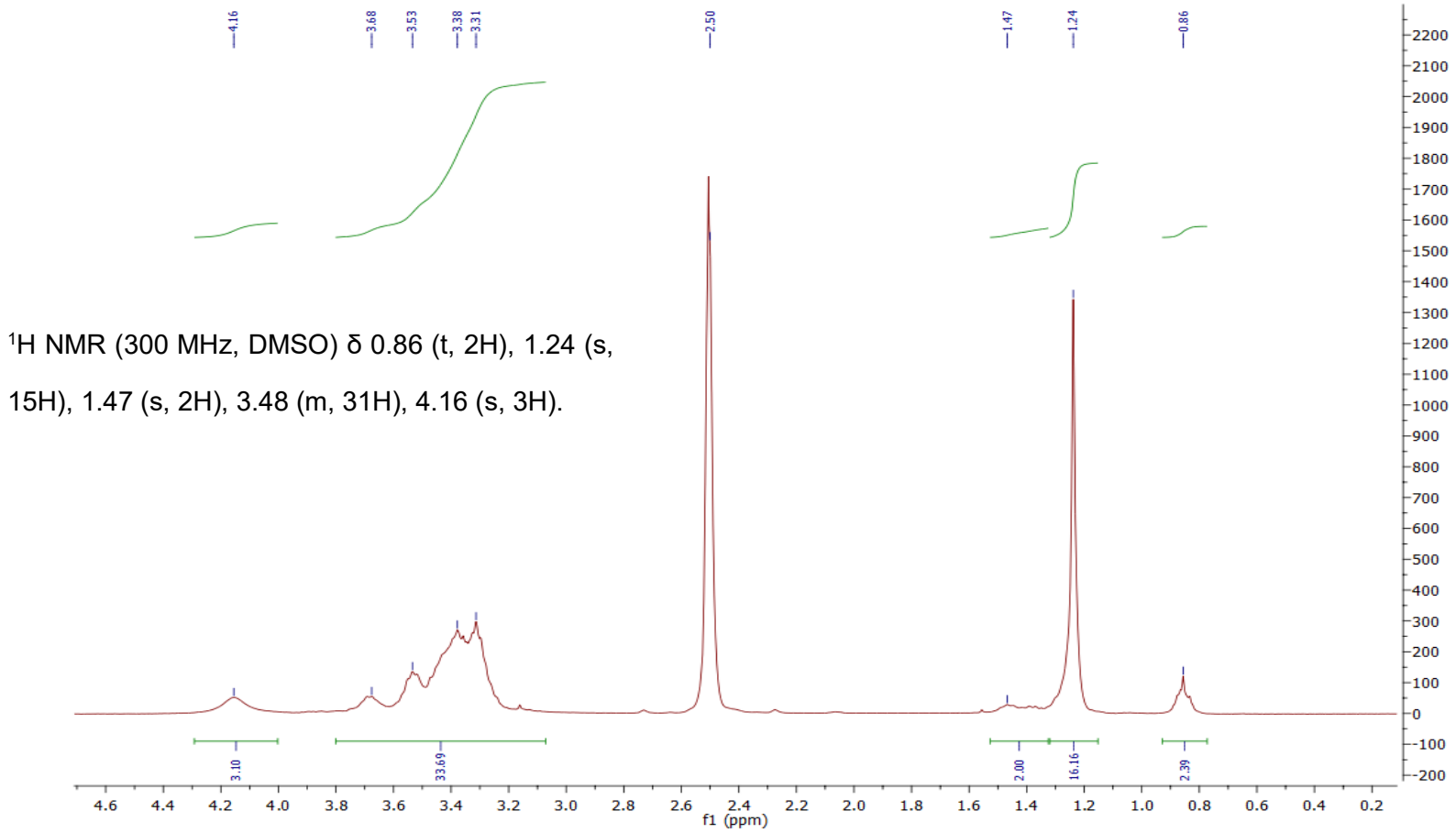


Figure 69 ^{1}H-NMR spectrum (dmso-d6) of surfactant C_9-Φ-G12



^{1}H NMR (300 MHz, DMSO) δ 0.86 (t, 2H), 1.24 (s, 15H), 1.47 (s, 2H), 3.48 (m, 31H), 4.16 (s, 3H).

Figure 70 ^{1}H-NMR spectrum (dmso-d_6) of surfactant C_{16}-12G

Table 26 The foaming test of polynonylphenol ethers

	G3		**G6**		**G10**		**G12**	
Mins.	Liquid vol. (ml)	Foam expansion	Liquid vol. (ml)	Foam expansion	Liquid vol. (ml)	Foam expansion	Liquid vol. (ml)	Foam expansion
1	19	1.368	16.8	3.274	17	3.588	17.9	3.911
2	19.3	1.347	17.4	3.161	17.9	3.408	18.7	3.743
3	19.4	1.340	17.8	3.090	18	3.389	18.9	3.704
4	19.6	1.327	17.9	3.073	18	3.389	18.9	3.704
5	19.8	1.313	17.9	3.073	18.1	3.370	18.9	3.704
10	19.9	1.307	18	3.056	18.2	3.352	18.9	3.704
15	20	1.300	18	3.056	18.3	3.333	18.9	3.704
	Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)	
	26		55		61		70	

Table 27 The foaming test of poly(glyceryl) ethers of octanol

	C_8-1G		**C_8-2G**		**C_8-3G**		**C_8-4G**		**C_8-5G**		**C_8-6G**		**C_8-9G**		**C_8-12G**	
Min	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.
1	16	2.50	16	4.25	15.	5.80	18.7	1.925	17.8	5.056	13.2	4.697	17.4	3.966	18	3.444
2	19	2.10	17.	3.79	17.	5.08	19.4	1.856	19	4.737	17.6	3.523	18.5	3.730	18.7	3.316
3	19.	2.05	18.	3.71	18.	4.86	19.9	1.809	19.2	4.688	19.2	3.229	18.6	3.710	18.9	3.280
4	19.	2.03	18.	3.63	18.	4.76	19.9	1.809	19.3	4.663	19.8	3.131	18.8	3.670	19	3.263
5	19.	2.02	18.	3.61	19	4.73	20	1.800	19.4	4.639	19.9	3.116	18.9	3.651	19	3.263
10	19.	2.02	19.	3.56	19.	4.68	20	1.800	19.7	4.569	20	3.100	19.2	3.594	19.1	3.246
15	19.	2.02	19.	3.48	19.	4.63	20	1.800	19.8	4.545	20	3.100	19.3	3.575	19.1	3.246
	Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)	
	40		68		90		36		90		62		69		48	

Table 28 The foaming test of poly(glyceryl) ethers of decanol

	C_{10}-1G		**C_{10}-3G**		**C_{10}-4G**		**C_{10}-5G**		**C_{10}-6G**		**C_{10}-9G**		**C_{10}-12G**	
Min.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.
1	13	3.462	17.2	2.5	16.8	3.33333	14	4.64285	15.1	4.63576	16.1	4.16149	16.8	4.76190
2	14.7	3.061	18.2	2.36263	17.2	3.25581	16.7	3.89221	17.8	3.93258	18	3.72222	18	4.44444
3	16.6	2.711	18.8	2.28723	17.8	3.14606	17.7	3.67231	18.8	3.72340	18.4	3.64130	18.2	4.39560
4	17.8	2.528	18.9	2.27513	18.1	3.09392	18	3.61111	19	3.68421	18.7	3.58288	18.4	4.34782
5	18.6	2.419	18.9	2.27513	18.2	3.07692	18.5	3.51351	19.1	3.66492	19	3.52631	18.5	4.32432
10	19.8	2.273	19.4	2.21649	18.7	2.99465	19.2	3.38541	19.4	3.60824	19.2	3.48958	18.8	4.25531
15	19.9	2.261	19.6	2.19387	18.9	2.96296	19.5	3.33333	19.5	3.58974	19.2	3.48958	19	4.21052
	Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)	
	45		43		56		65		70		67		80	

Table 29 The foaming test of poly(glyceryl) ethers of dodecanol

	C_{12}-1G		**C_{12}-3G**		**C_{12}-6G**		**C_{12}-9G**		**C_{12}-12G**	
Mins.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.	Liq. vol. (ml)	Foam exp.
1	18	1.611	8	7.875	9.9	5.859	9.8	6.327	11.3	5.752
2	18	1.611	12.7	4.961	12.9	4.496	12.5	4.960	14.2	4.577
3	18	1.611	13.8	4.565	14.2	4.085	14.2	4.366	15.8	4.114
4	18	1.611	14.6	4.315	15.1	3.841	15.1	4.106	16.5	3.939
5	18	1.611	15.1	4.172	15.9	3.648	15.9	3.899	17	3.824
10	18.1	1.602	15.9	3.962	17.2	3.372	17.5	3.543	18.2	3.571
15	18.2	1.593	16.5	3.818	17.9	3.240	18	3.444	18.9	3.439
	Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)		Foam (ml)	
	29		63		58		62		65	

7 References

[1] *Statistical Review of World Energy. (2017). bp.com.* Retrieved 12 October 2017, from https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html

[2] Demirbas, A. (2007). Importance of biodiesel as transportation fuel. *Energy Policy*, 35(9), pp.4661-4670.

[3] Karaosmanoğlu, F., Cığızoğlu, K., Tüter, M. and Ertekin, S. (1996). Investigation of the Refining Step of Biodiesel Production. *Energy & Fuels*, 10(4), pp.890-895

[4] Maru, B., López, F., Kengen, S., Constantí, M. and Medina, F. (2016). Dark fermentative hydrogen and ethanol production from biodiesel waste glycerol using a co-culture of Escherichia coli and Enterobacter sp. *Fuel*, 186, pp.375-384.

[5] Adoption of the Paris Agreement. Proposal by the President., FCCC/CP/2015/L.9/Rev.1, *United Nations Office*, *Geneva, Switzerland,* 2016.

[6] Zakaria, Z., Linnekoski, J. and Amin, N. (2015). Catalyst screening for conversion of glycerol to glycerol carbonate. *Chemical Engineering Journal*, 207-208, pp.803-813.

[7] *Glycerol Market- Global Industry Analysis, Size, Growth and Forecast 2012-2018.* (2017). Transparencymarketresearch.com. Retrieved 12 October 2017, from https://www.transparencymarketresearch.com/glycerol.market.html

[8] Markočič, E., Kramberger, B., van Bennekom, J., Jan Heeres, H., Vos, J., & Knez, Ž. (2013). Glycerol reforming in supercritical water; a short review. *Renewable And Sustainable Energy Reviews*, 23, pp.40-48.

[9] Kuehner, M. (2016). *Surfactants – Study: Market, Analysis, Trends* | *Ceresana*. [online] Ceresana.com. Available at: http://www.ceresana.com/en/market-studies/chemicals/surfactants [Accessed 28 Nov. 2016]

[10] Reznik, G., Vishwanath, P., Pynn, M., Sitnik, J., Todd, J., Wu, J., Jiang, Y., Keenan, B., Castle, A., Haskell, R., Smith, T., Somasundaran, P. and Jarrell, K. (2010). Use of sustainable chemistry to produce an acyl amino acid surfactant. *Applied Microbiology and Biotechnology*, 86(5), pp.1387-1397.

[11] Katepalli, H., Bose, A., Hatton, T. and Blankschtein, D. (2016). Destabilization of Oil-in-Water Emulsions Stabilized by Non-ionic Surfactants: Effect of Particle Hydrophilicity. *Langmuir*, 32(41), pp.10694-10698.

[12] Gaudin, P., Jacquot, R., Marion, P., Pouilloux, Y., & Jérôme, F. (2011). Acid-Catalyzed Etherification of Glycerol with Long-Alkyl-Chain Alcohols. *Chemsuschem,* 4(6), 719-722.

[13] Gaudin, P., Jacquot, R., Marion, P., Pouilloux, Y., & Jérôme, F. (2011). Homogeneously-catalyzed etherification of glycerol with 1-dodecanol. Catalysis Science & Technology, 1(4), 616.

[14] SICHUAN LUTIANHUA COMPANY LIMITED (2015). *Catalyst and method preparing dimethyl carbonate by using catalyst.* CN105251496 (A).pp.1-1.

[15] Ochoa-Gómez, J., Gómez-Jiménez-Aberasturi, O., Ramírez-López, C., & Belsué, M. (2012). A Brief Review on Industrial Alternatives for the Manufacturing of Glycerol Carbonate, a Green Chemical. Organic Process Research & Development, 16(3), 389-399.

[16] GLYCIDOL. (2017). *Pubchem.ncbi.nlm.nih.gov.* Retrieved 18 October 2017, from https://pubchem.ncbi.nlm.nih.gov/compound/glycidol#section=Color

[17] Sulimov, A., Danov, S., Ovcharova, A., Ovcharov, A., & Flid, V. (2014). Regularities of glycidol synthesis by the liquid-phase epoxidation of allyl alcohol with hydrogen peroxide. Russian Chemical Bulletin, 63(12), 2647-2651.

[18] Robert, M. H. (1991) The synthetic methodology of nonracemic glycidol and related 2,3-epoxy alcohols. *Chem. Rev.* 1991, 91 (4), pp 437–475.

[19] Zhou, Y., Ouyang, F., Song, Z., Yang, Z. and Tao, D. Catal. Commun., 2015, 66, p.25-29.

[20] Hanson, R. (1991). The synthetic methodology of nonracemic glycidol and related 2,3-epoxy alcohols. *Chemical Reviews*, 91(4), pp.437-475.

[21] Bolívar-Diaz, C., Calvino-Casilda, V., Rubio-Marcos, F., Fernández, J. and Bañares, M. (2013). New concepts for process intensification in the conversion of glycerol carbonate to glycidol. *Applied Catalysis B: Environmental*, 129, pp.575-579.

[22] Choi, J., Simanjuntaka, F., Oh, J., Lee, K., Lee, S., Cheong, M., Kim, H. and Lee, H. (2013). Ionic-liquid-catalyzed decarboxylation of glycerol carbonate to glycidol. *Journal of Catalysis*, 297, pp.248-255.

[23] Hine, C.H., Kodama, J.K., Wellington, J.S., Dunlap, M.K. & Anderson H.H. (1956). The toxicology of glycidol and some glycidyl ethers. Arch. ind. *Health*, 14, 250–264.

[24] Proctor, N.H. & Hughes, J.P. (1989). Chemical Hazards of the Workplace, *Philadelphia, PA, Lippincott*, pp. 276.

[25] Ivashkiv, E. & Dunham, J.M. (1973). Determination of trace amounts of glycidol in milk of magnesia. J. *pharm. Sci*., 62,pp. 285–287.

[26] Kleemann, A.; Wagner, R. M. (1981) *Glycidol; Hüthig*: New York, 1981.

[27] Hanson, R. M. (1991) The synthetic methodology of nonracemic glycidol and related 2,3-epoxy alcohols. *Chemical Reviews* 1991, 91, 437.

[28] Sienel, G., Rieth, R. & Rowbottom, K.T. (1999). Ullmann's Encyclopedia of Chemical Technology, 5th rev. Ed., Vol. A9, New York, *VCH Publishers,* pp. 541.

[29] Hooper, K., LaDou, J., Rosenbaum, J.S. & Book, S.A. (1992). Regulation of priority carcinogens and reproductive or developmental toxicants. *Am. J. ind. Med*., 22, pp.793–808.

[30] American Conference of Governmental Industrial Hygienists (1986) Documentation of the Threshold Limit Values and Biological Exposure Indices, 5th Ed., *Cincinnati, OH, ACGIH*®,pp. 287.

[31] Ann, T. (1997) Dow Chemical opens new GMA plant. *Chem. Eng. News*, 1997, *75* (9), pp. 26.

[32] Farn, R. (2006). Chemistry and technology of surfactants. 1st ed. Oxford: Blackwell Pub., pp.22-23.

[33] (2017). 163.com. Retrieved 28 September 2017, from http://home.henan.163.com/17/08/09/CMSHBOMOXY703788.html

[34] Physical Chemistry Laboratory. (2017). Tau.ac.il. Retrieved 30 September 2017, from https://www.tau.ac.il/~phchlab/experiments_new/surface_tenstion/theory.html

[35] Surfactant Classification. (2017). Cosmetics.specialchem.com. Retrieved 28 September 2017, from http://cosmetics.specialchem.com/selection-guide/selection-guide-cleansing-hair-and-skin/surfactant-classification

[36] Kunjappu, J., & Rosen, M. (2013). *Surfactants and interfacial phenomena*. *Hoboken*, N.J.: Wiley. pp. 19-32.

[37] Market scope expanded for synthetic-alcohol non-ionic surfactants. (2010). *Focus on Surfactants*, 2010(12), pp.4.

[38] Shigeta, K.Olsson, U. Kunida, H. (2001) Correlation between Micellar Structure and Cloud Point in Long Poly(oxyethylene)n Oleyl Ether Systems. *Langmuir*, 2001,17: pp.4717-4723.

[39] Furlong, D. and Aston, J. (1982) Adsorption of polyoxyethylated nonyl phenols at silica/aqueous solution interfacesOriginal Research Article. *Colloids Surf*, 1982,4:pp.121-129.

[40] Attwood, D., & Florence, A. (2013). Physical pharmacy. London: *Pharmaceutical Press*. pp. 43-48.

[41] *CMC.* (2017). *Kruss.de*. Retrieved 28 September 2017, from https://www.kruss.de/services/education-theory/glossary/cmc/

[42] Salem, J., El-Nahhal, I., Najri, B., Hammad, T. and Kodeh, F. (2016). Effect of anionic surfactants on the surface plasmon resonance band of silver nanoparticles: Determination of critical micelle concentration. *Journal of Molecular Liquids*, 223, pp.771-774.

[43] Butt, H., Graf, K.and Kappl, M. (2006). Physics and chemistry of interfaces (2., rev. and enl. ed.). Weinheim: *Wiley-VCH-Verl.* p.16.ISBN 9783527406296.

[44] What is Surface Tension? :Kyowa Interface Science. (2017). Face-kyowa.co.jp. Retrieved 3 October 2017, from http://www.face-kyowa.co.jp/english/en_science/en_theory/en_what_Surface_tension/

[45] Butt, H., Graf, K., Kappl, M. (2003). "*Physics and Chemistry of Interfaces*": pp.14–15.

[46] Lavkush, M., Pandey, S., Shahnawaz, M., Talib, A. and Wu, H. (2015). Fluorophotometric determination of critical micelle concentration (CMC) of ionic and non-ionic surfactants with carbon dots via Stokes shift. *Talanta*, 132, pp.572-578.

[47] Prazeres, T., Beija, M., Fernandes, F., Marcelino, P., Farinha, J. and Martinho, J. (2012). Determination of the critical micelle concentration of surfactants and amphiphilic block copolymers using coumarin 153. Inorganica *Chimica Acta*, 381, pp.181-187.

[48] Vargaftik, N., Volkov, B., & Voljak, L. (1983). International Tables of the Surface Tension of Water. *Journal Of Physical And Chemical Reference Data*, 12(3), pp.817-820.

[49] Griffin, W. C. (1949). Classification of Surface-Active Agents by 'HLB', *Journal of the Society of Cosmetic Chemists*, 1 (5): pp.311-26.

[50] Griffin, W. C. (1954). Calculation of HLB Values of Non-Ionic Surfactants, Journal of the Society of Cosmetic *Chemists*, 5 (4): pp.249-56.

[51] Davies, J. T. (1957). A quantitative kinetic theory of emulsion type, I. Physical chemistry of the emulsifying agent. *Surface Activity*.2 (1): pp.426 -438.

[52] Huang, Y., Qin, W., Huo, X., et al. Surfactant distribution in the clouding of C12E10. Colloids and Surfaces A: *Physicochem Eng* Aspects, 2006, 276: pp. 228~231.

[53] Schott H. Tenside Surf. Study on Cloud Point of Non-ionic Surfactant, *Det*., 1996, 33 (6) : pp.457 ~ 463.

[54] Huang. Y., Qin. W., Dai. L. Turbidity extraction technology and its application in separation process [J]. *Modern chemical*, 2006, 26 (supplement) : pp.307 ~ 309.

[55] Xiao J X, Sivars U, Tjerneld F. Phase behavior and protein partitioning in aqueous two-phase systems of cationic-anionic surfactant mixtures [J]. J *Chromatogr B*, 2000, 743: pp.327~338.

[56] Reif I, Mulqueen M, Blankschtein D. Molecular-thermodynamic prediction of critical micellar concentrations of commercial surfactants [J]. *Langmuir*, 2001, 17:pp. 5801~5812.

[57] Huang. Y., Qin. W., Liu. H. Non-ionic surfactant C12E10 turbid point phase behavior and its application [J]. Journal of chemical engineering, 2007, 58 (5) : pp.1253 ~ 1258.

[58] Surface Active Agents (Surfactants): Types and Applications. (2017). *Prospector Knowledge Center*. Retrieved 12 October 2017, from https://knowledge.ulprospector.com/3106/pc-surface-active-agents-surfactants/

[59] *Gibb's Adsorption Isotherm.* (2017). Retrieved 12 October 2017, from http://image.sciencenet.cn/olddata/kexue.com.cn/bbs/upload/1367103_lect_Gibbs_Adsorption_-_Fall_2006_SC.pdf

[60] Study on Foaming Property of Surfactant. (2017). Kodi.cn. Retrieved 28 September 2017, from http://www.kodi.cn/GetKnowledge/zh-cn/p496_k651.aspx?PrintFriendly=true

[61] Rosen, M., & Solash, J. (1969). Factors affecting initial foam height in the Ross-Miles foam test. Journal Of The American Oil Chemists' Society, 46(8), 399-402.

[62] ASTM D1173 − 07 (Reapproved 2015): Standard Test Method for Foaming Properties of Surface-Active Agents.

[63] Evaluation of wild land fire chemicals (2017). Retrieved 26 September 2017, from https://www.fs.fed.us/t-d/programs/wfcs/wfcs/tests/documents/stp_08_3.pdf

[64] Christian, S. & Scamehorn, J. (1995). Solubilization in surfactant aggregates. 1st ed. New York: Marcel Dekker, pp.21-25.

[65] Tyagi, P. and Tyagi, R. (2009). Synthesis, Structural Properties and Applications of Gemini Surfactants: A Review. Tenside Surfactants Detergents, 46(6), pp.373-382.

[66] Melamid, A. (1955). Geographical Distribution of Petroleum Refining Capacities: A Study of the European Refining Program. Economic Geography, 31(2), p.168.

[67] Goon, P., Bhirud, R. and Kumar, V. (1999). Detergency and foam studies on linear alkylbenzene sulfonate and secondary alkyl sulfonate. Journal of Surfactants and Detergents, 2(4), pp.489-493.

[68] Lappin, G. and Sauer, J. (1989). Alpha olefins applications handbook. 1st ed. New York: M. Dekker, p.243.

[69] Os, N. (1998). Non-ionic surfactants. 1st ed. New York, N.Y.: Marcel Dekker.

[70] (2017). Retrieved 18 October 2017, from https://application.wiley-vch.de/books/sample/3527306293_c01.pdf

[71] *Surfactants Market by Type, Substrate, Application & by Geography - 2021 | MarketsandMarkets.* (2017). Marketsandmarkets.com. Retrieved 26 September 2017, from http://www.marketsandmarkets.com/Market-Reports/biosurfactants-market-493.html

[72] Patrick, J., Kinlen, Vinod, P., Menon, P., *Cholesterol reducing sterol compositions, preparation and method of use*. (2000). EP 1225812 A2.

[73] Murai, T. (2005). Synthesis and Reactions of Selenothioic Acid S -Esters and Diselenoic Acid Esters. *Synlett,* (10), pp.1509-1520.

[74] Verma, R. and Gehlawat, J. (2007). Kinetics of hydrogenation of D-glucose to sorbitol. *Journal of Chemical Technology & Biotechnology*, 46(4), pp.295-301.

[75] Martino, D. S., Riccardo, T. and Santacesaria, E. (2005). "Comparison of Different Reactor Types Used in the Manufacture of Ethoxylated, Propoxylated Products". *Industrial & Engineering Chemistry Research*. 44 (25), pp. 9482–9489.

[76] *Levelling Agent O-20，CAS number, use, process, physical and chemical properties，Chemical Dictionary - ChemNet.* (2017). Anychem.com. Retrieved 29 September 2017, from http://www.anychem.com/dict/detail/ziFzqi.html

[77] Garcia, J. I. Garcia-Marin, H. J. Mayoral, A. Perez, P. Green Chem. 2010, 12, pp.426–434.

[78] Xie, F. and Zhu, C. Synthesis of Polyethylene Glycol. *Chemical Propellants & Polymeric Materials*, 3(4), pp. 6-8.

[79] Fan, Z., Zhao, Y., Preda, F., Clacens, J., Shi, H., & Wang, L. et al. (2015). Preparation of bio-based surfactants from glycerol and dodecanol by direct etherification. *Green Chem.*, 17(2), 882-892.

[80] Gaudin, P., Jacquot, R., Marion, P., Pouilloux, Y., & Jérôme, F. (2011). Acid-Catalyzed Etherification of Glycerol with Long-Alkyl-Chain Alcohols. *Chemsuschem,* 4(6), 719-722.

[81] Gaudin, P., Jacquot, R., Marion, P., Pouilloux, Y., & Jérôme, F. (2011). Homogeneously-catalyzed etherification of glycerol with 1-dodecanol. *Catalysis Science & Technology*, 1(4), 616.

[82] Parvulescu, A. N., P. Hausoul J. C., Bruijnincx, P. C. A., Klein Gebbink R. J. M. and Weckhuysen, B. M., Catal. *Today*, 2010, 158, 130–138.

[83] Parvulescu, A. N., Mores, D., Stavitski, E., Teodorescu, C. M., Bruijnincx, Gebbink, P. C., A. R. J. M. K. and Weckhuysen, B. M. Am, J., *Chem*. Soc., 2010, 132, 10429–10439.

[84] Ruppert, A. M., Parvulescu, A. N., Arias, M. P. Hausoul, J. C. Bruijnincx, P. C. A., Klein Gebbink R. J. M. and Weckhuysen, B. M. J. *Catal.*, 2009, 268, 251–259.

[85] Sutter, M., Dayoub, W., Métay, E., Raoul, Y. and Lemaire, M. (2012). Selective Synthesis of 1- O -Alkyl(poly)glycerol Ethers by Catalytic Reductive Alkylation of Carboxylic Acids with a Recyclable Catalytic System. *ChemSusChem*, 5(12), pp.2397-2409.

[86] Fan, Z., Zhao, Y., Preda, F., Clacens, J., Shi, H., Wang, L., Feng, X. and De Campo, F. (2015). Preparation of bio-based surfactants from glycerol and dodecanol by direct etherification. *Green Chem.,* 17(2), pp.882-892.

[87] Urata, K. and Takaishi, N. (1998). Applications of protecting groups in the synthesis of surfactants, lipids, and related compounds. Journal of Surfactants and Detergents, 1(1), pp.73-82.

[88] Urata, K., Yano, S., Kawamata, A., Takaishi, N. and Inamoto, Y. (1988). A convenient synthesis of long-chain 1-O-Alkyl glyceryl ethers. Journal of the American Oil *Chemists Society*, 65(8), pp.1299-1302.

[89] Wolfgang Beilfuss, (2011). *Process for the preparation of 1-alkyl glycerol ethers.* US20110009676 A1.

[90] Akira Wakayama. *Process for producing Polyglycerol ether derivative*. EP 1958929 B1.

[91] Sutter, M., Silva, E., Duguet, N., Raoul, Y., Métay, E. and Lemaire, M. Glycerol Ether Synthesis: A Bench Test for Green Chemistry Concepts and Technologies. *Chemical Reviews*, 115(16), pp.8609-8651.

[92] Akira, S., Kao Corporation. (2012). *Process for producing polyglyceryl ether derivative.* EP 1 958 929 B1.

[93] Rhodia Operations, (2015). *Method for preparing glycerol ether and glycol ether.* EP 2828230 A1.

[94] Mignani, G., Lemaire, M. and Eric Da, S. (2013). Method for preparing glycerol ether and glycol ether. WO 2013139995 A1.

[95] Dow introduces Ecosurf LF APEO-free pigment grind surfactant. (2011). Focus on surfactants, 2011(7), pp. 3.

[96] Nonylphenol Ethoxylate Surfactants. (2015). Product Safety Assessment: DOW™ *Nonylphenol Ethoxylate Surfactants*, 21, 10, 2015, pp.1-8.

[97] Kao Corporation, (2014). Process for the preparation of polyglyceryl ether derivatives. US 8,822,735 B2.

[98] Raymond, M., and Scardera, M. (1973). Alkali-halogenated solvent emulsion system. US 3723341 A.

[99] Behr, A., Eilting, J., Irawadi, K., Leschinski, J., & Lindner, F. (2008). Improved utilisation of renewable resources: New important derivatives of glycerol. Green Chem., 10(1), 13-30. http://dx.doi.org/10.1039/b710561d

[100] Vera L. P. Soares, Elizabeth R. Lachter, Jorge de A. Rodrigues Jr, Luciano N. Batista, & Regina S. V. Nascimento. (2011). New Applications for Soybean Biodiesel Glycerol. INTECH Open Access Publisher.

[101] The present invention relates to a process for producing polyglyceryl ether derivatives. (2007). WO 2007/066723 (14.06.2007 Gazette 2007/24).

[102] Rai, A. and Basu, A. (2003). An Efficient Method for para-Methoxybenzyl Ether Formation with Lanthanum Triflate. *ChemInform*, 34(22).

[103] A quantitative kinetic theory of emulsion type. i. physical chemistry of the emulsifying agent. (1957). 1st ed. london: *Gas/Liquid and Liquid/Liquid Interfaces*, pp.430-431.

[104] Foaming Ability. (2016). [ebook] Evaluation of wildland fire chemicals, pp.1-1. Available at: https://www.fs.fed.us/rm/fire/wfcs/tests/documents/stp_08_3.pdf [Accessed 2 Aug. 2017].

[105] Sutter, M., Silva, E., Duguet, N., Raoul, Y., Métay, E. and Lemaire, M. Glycerol Ether Synthesis: A Bench Test for Green Chemistry Concepts and Technologies. *Chemical Reviews*, 115(16), pp.8609-8651.

[106] George, J. L.& Kenneth, C. R., Jefferson Chemical Company. (1976). *Anhydrous catalyst for manufacture of glycol ethers*. Amarica. US3972948 A

[107] Gioacchino, C. & Benedetto, C., Societa'italiana Resine S.I.R. S.P.A. (1976). *Process for the production of glycol ethers*. America. US 3935279 A

[108] Zhang, Y., You, Q., Fu, Y., Zhao, M., Fan, H., Liu, Y., & Dai, C. (2016). Investigation on interfacial/surface properties of bio-based surfactant N-aliphatic amide-N, N-diethoxypropylsulfonate sodium as an oil displacement agent regenerated from waste cooking oil. Journal Of Molecular Liquids, 223, 68-74.

[109] Physical Pharmacy (2017). Retrieved 11 October 2017, from https://www.pharmpress.com/files/docs/FTphyspharm_sample.pdf

[110] Nonylphenol Ethoxylates (NPE). (2017). Dow.com. Retrieved 28 September 2017, from http://www.dow.com/surfactants/products/nonylph.htm

[111] Holmberg, K., Jönsson, B. Kronberg, B. and Lindman, B. (2002) “Surfactants and Polymers in Aqueous Solution, Chapter 2: surfactant micellization”, John Wiley & Sons Ltd., *Chichester*, England.

[112] Rammohan, P. Amberlyst-15 in organic synthesis. (2012). *Arkivoc*, 2012(1), pp. 570. http://dx.doi.org/10.3998/ark.5550190.0013.114 3

[113] Iwanami, K., Yano, K., & Oriyama, T. (2007). Iron(III) Chloride Catalyzed Reductive Etherification of Carbonyl Compounds with Alcohols. *Cheminform*, 38(26).

[114] Krogh, K., Halling-Sørensen, B., Mogensen, B., & Vejrup, K. (2003). Environmental properties and effects of non-ionic surfactant adjuvants in pesticides: a review. *Chemosphere*, 50(7), pp. 871-901.

[115] Kato, T., Nakamura, T., Yamashita, M., Kawaguchi, M., Kato, T., & Itoh, T. (2003). Surfactant properties of purified polyglycerol monolaurates. *Journal of Surfactants And Detergents*, 6(4), pp.331-337.

[116] The determination method and influencing factors of CMC. (2017). Wenku.baidu.com. Retrieved 11 October 2017, from https://wenku.baidu.com/view/5b1fe0f6f61fb7360b4c65d9.html

[117] Jinping, W. & Tiren, G., Effect of Added Electrolytes on the Cloud Point of Non-ionic Surfactant Solutions. *Acta Physico-Chimica Sinica*, 1996, 12(11): pp. 965-970.

[118] *BASF - Product Information BASF Chemicals NAFTA - Lutensol® XP 90.* (2017). Worldaccount.basf.com. Retrieved 12 October 2017, from https://worldaccount.basf.com/wa/NAFTA/Catalog/ChemicalsNAFTA/info/BASF/PRD/30149371